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Monsanto Research Corp, Dayton, Ohio

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SOURCE ASSESSMENT: PESTICIDE MANUFACTURING AIR EMISSIONS- OVERVIEW AND PRIORITIZATION

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The report is an overview of the pesticide manufacturing industry and prioritizes 80 major pesticides based on their potential environmental burden from an air pollution standpoint. Production of synthetic organic pesticides was about 640,000 metric tons in 1974. Thirty-seven major synthetic organic pesticides, those with annual production of 4540 or more tons, accounted for 74% of the market. Elemental chlorine is common to most pesticides, but other raw materials include hydrogen cyanide, carbon disulfide, phosgene, phosphorus pentasulfide, hexachlorocyclopentadiene, various amines, and concentrated acids and caustics. Air pollution aspects of the pesticide manufacturing industry are essentially without quantitative data. For some plants, the pollution caused by loss of active ingredients is less significant than that caused by unreacted by-products. Evaporation from holding ponds and evaporation lagoons may also be an emission source, although few quantitative data are available. Emissions emanate from various pieces of equipment and enter the atmosphere as both the active ingredient and as raw materials, intermediates, and by-products. Air emission control devices include baghouses, cyclone separators, electrostatic precipitators, incinerators, and gas scrubbers. Synthetic organic pesticide production in 1985 will be about 806,000 metric tons.

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Industrial Processes, Lagoons	Source Assessment	13H, --
Gas Filters, Cyclone Separators	Emission Factors	13K, 07A
Electrostatic Precipitators, Incinerators	Baghouses	
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PREFACE

The Industrial Environmental Research Laboratory (IERL) of the U.S. Environmental Protection Agency (EPA) has the responsibility for insuring that pollution control technology is available for stationary sources to meet the requirements of the Clean Air Act, the Federal Water Pollution Control Act and solid waste legislation. If control technology is unavailable, inadequate, or uneconomical, then financial support is provided for the development of the needed control techniques for industrial and extractive process industries. The Chemical Processes Branch of the Industrial Processes Division of the IERL has the responsibility for investing tax dollars in programs to develop control technology for a large number of operations (greater than 500) in the chemical industries.

Monsanto Research Corporation (MRC) has contracted with EPA to investigate the environmental impact of various industries which represent sources of pollution in accordance with EPA's responsibility as outlined above. Dr. Robert C. Binning serves as MRC Program Manager in this overall program entitled "Source Assessment," which includes the investigation of sources in each of four categories: combustion, organic materials, inorganic materials, and open sources. Dr. Dale A. Denny of the Industrial Processes Division at Research Triangle Park serves as EPA Project Officer. Reports prepared in this program are of three types: Source Assessment Documents, State-of-the-Art Reports, and Special Project Reports.

Source Assessment Documents contain data on emissions from specific industries. Such data are gathered from the literature, government agencies and cooperating companies. Sampling and analysis are also performed by the contractor when the available information does not adequately characterize the source emissions. These documents contain all of the information necessary for IERL to decide whether a need exists to develop additional control technology for specific industries.

State-of-the-Art Reports include data on emissions from specific industries which are also gathered from the literature, government agencies and cooperating companies. However, no extensive sampling is conducted by the contractor for such industries. Results from such studies are published as State-of-the-Art Reports for potential utility by the government, industry, and others having specific needs and interests.

Special projects provide specific information or services which are applicable to a number of source types or have special utility to EPA but are not part of a particular source assessment study. This special project report, "Source Assessment: Pesticide Manufacturing Air Emissions - Overview and Prioritization," was prepared to provide a general summary of pesticide manufacturing, and to furnish information on individual pesticide source types. Mr. David K. Oestreich of IERL-RTP served as EPA Task Officer.

ABSTRACT

This report provides an overview of the pesticide manufacturing industry and a prioritization listing of 80 major pesticides based upon their potential environmental burden from an air pollution standpoint. Production of synthetic organic pesticides is estimated to have been 6.4 x 10^5 metric tons in 1974. Thirty-seven major synthetic organic pesticides, those with annual production greater than or equal to 4,540 metric tons, accounted for 74% of the market. The raw material most commonly used in pesticide manufacturing is elemental chlorine, but other raw materials include hydrogen cyanide, carbon disulfide, phosgene, phosphorus pentasulfide, hexachlorocyclopentadiene, various amines, and concentrated acids and caustics.

Air pollution aspects of the pesticide manufacturing industry are essentially without quantitative data. For some plants, the pollution caused by loss of active ingredient is less significant than that caused by unreacted byproducts. Evaporation from holding ponds and evaporation lagoons may also be an emission source, although few quantitative data are available. Emissions, including particulates, gases, and vapors from the manufacturing process, emanate from various pieces of equipment (for example, reactors, driers, and condensers) and enter the atmosphere as both the active ingredient and as raw materials, intermediates, and byproducts. Air emission control devices include baghouses, cyclone separators, electrostatic precipitators, incinerators, and gas scrubbing units. Based on an estimated 1% annual growth rate, total synthetic organic pesticide production in 1985 will be approximately 8.06 x 10^5 metric tons.

Toxaphene ranked highest among the 80 pesticides prioritized. The listing points out the potential environmental burden due to evaporation from holding ponds and evaporation lagoons, and due to sulfur dioxide emissions from flaring and incinerating sulfur containing compounds.

This report was submitted in partial fulfillment of Contract No. 68-02-1874 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. The study described in this report covers the period July 1976 to January 1978.

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ABBREVIATIONS AND SYMBOLS

A -- surface area

C_i -- concentration of pesticide "i" at time t

C_{io} -- initial concentration of pesticide "i"

C_{is} -- saturation concentration of pesticide "i"

C_1 -- total ammoniacal nitrogen at time t_1

C_2 -- total ammoniacal nitrogen at time t_2

e -- 2.72

E -- water evaporation rate

F -- hazard factor

F_i -- environmental hazard potential factor of the ith material

F_r -- ratio of undissociated ammonia to the total ammoniacal nitrogen in solution

G -- weight of body of water

h -- stack height

I_x -- impact factor

K_D -- operational desorption coefficient

K_x -- number of sources emitting materials associated with source type x

m_A -- mass of ammonia desorbing from pond or lagoon

m_i -- mass of material "i" evaporating from pond or lagoon

M_w -- molecular weight of water

M_i -- molecular weight of "i"

N -- number of materials emitted by each source

P_{is} -- vapor pressure of pure solid or liquid "i"

P_j -- population density in the region associated with the jth source

P_w -- vapor pressure of water

Q -- emission rate

S_i -- corresponding standard for the ith material (used only for criteria emissions, otherwise set equal to one)

ABBREVIATIONS AND SYMBOLS (continued)

t -- time

t_a -- averaging time

t_{HR} -- hydraulic retention time

TKN -- total Kjeldahl nitrogen

TLV -- threshold limit value

t_o -- instantaneous averaging time

u -- wind speed

UL -- uncertainty level

V -- volume of water body

θ -- temperature

π -- 3.14

χ'_{ij} -- ambient concentration of the ith material in the region associated with the jth source

$\bar{\chi}_{ij}$ -- calculated time-averaged maximum ground level concentration of the ith material emitted by the jth source

χ_{max} -- instantaneous (i.e., 3-min average) maximum ground level concentration

$\bar{\chi}_{max}$ -- maximum time-averaged ground level concentration

SECTION 1

INTRODUCTION

Pesticide chemical manufacturing results in air emissions, but too few quantitative data are available to determine whether sufficient pollution control technology is available. Due to this lack of emissions data, an industry overview and emissions source prioritization model was necessary to furnish information regarding major pesticide chemicals. This report provides an industry overview and prioritization of mass emissions from pesticide chemical manufacturing in order to permit selection of specific pollution sources for detailed assessment.

Contained in the industry overview is a description of the scope of the pesticide manufacturing industry in terms of process operations, raw materials, final products, and production trends. The industry is then divided into 12 segments for air emissions evaluation and source prioritization. Quantitative emissions data are presented where available. Estimates of emission species and emission factors are determined from raw materials used, process chemistry, and unit operations where quantitative emissions data are unavailable.

Environmental impact factors are determined from the emissions data for 80 pesticide chemical manufacturing source types. These source types are then rank ordered, by pesticide chemical, with regard to their commonly described potential hazard to the environment from an air pollution standpoint.

SECTION 2

SUMMARY

A pesticide is defined as 1) any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest, or 2) any substance intended for use as a plant regulator, defoliant, or desiccant. The pesticide manufacturing industry with its associated sources of emissions is represented schematically in Figure 1. Production of synthetic organic pesticides is estimated to have been 6.4×10^5 metric tons in 1974. The pesticide manufacturing industry is dominated by a small number of major products, while a large number of minor products compete for a small share of the market. Thirty-seven major synthetic organic pesticides, those with annual production greater than or equal to 4,540 metric tons, accounted for 74% of the market in 1974. The remaining 26% of production was divided among about 300 other pesticides.

In 1976, there were 139 pesticide manufacturing plants (excluding industrial chemicals with minor pesticide uses, which are primarily products of other industries) distributed throughout 34 states in the United States. These plants generally employ unit operations and equipment similar to those used by the chemical processing industry (reaction kettles, driers, filters, etc.). The raw material common to the most pesticides is elemental chlorine, which is used directly on site in the production of chlordane, toxaphene, 2,4-D, 2,4,5-T, atrazine, captan, carbaryl, and mercuric chloride. Chlorine is also used to prepare raw materials brought in for production of DDT, aldrin, and perhaps trifluralin and alachlor. Raw materials of an unusually hazardous nature include hydrogen cyanide, carbon disulfide, various amines, and concentrated acids and caustics. The phosphorus pentasulfide (P_2S_5) used in manufacturing organophosphorus pesticides, the hexachlorocyclopentadiene (C_5Cl_6) used for cyclodiene pesticides, the phosgene used to make carbaryl, and numerous other raw materials, as well as solvents such as xylene, toluene, and similar materials, present potential health hazards.

Air pollution aspects of the pesticide manufacturing industry are essentially without quantitative data. For some plants, the pollution caused by loss of active ingredient is less significant than that caused by unreacted byproducts such as hydrogen sulfide (H_2S), which is flared to form sulfur dioxide (SO_2), or particulates resulting from fuel combustion. A plant producing

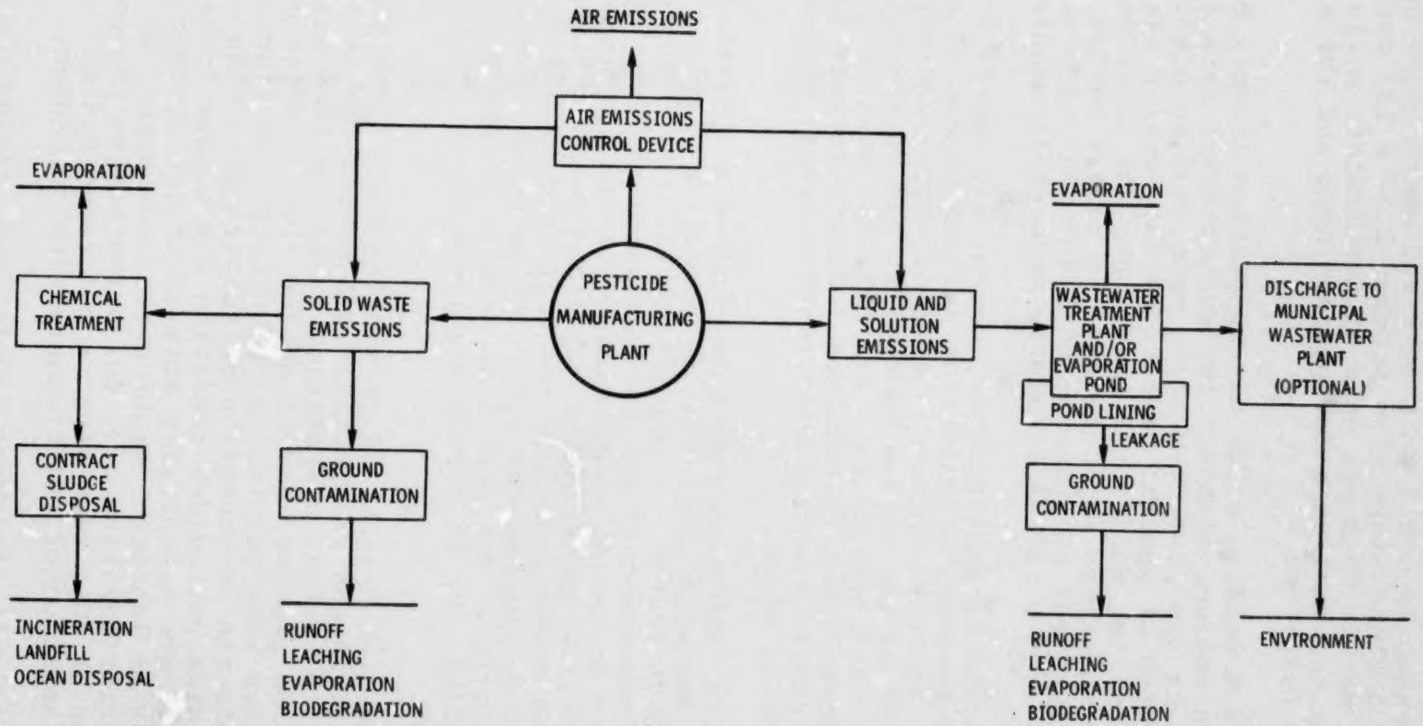
AIR EMISSIONS
AIR EMISSIONS CONTROL DEVICE
EVAPORATION
CHEMICAL TREATMENT
SOLID WASTE EMISSIONS
PESTICIDE MANUFACTURING PLANT
LIQUID AND SOLUTION EMISSIONS
EVAPORATION
WASTEWATER TREATMENT PLANT AND/OR EVAPORATION POND
POND LINING
LEAKAGE
DISCHARGE TO MUNICIPAL WASTEWATER PLANT (OPTIONAL)
CONTRACT SLUDGE DISPOSAL
GROUND CONTAMINATION
GROUND CONTAMINATION
INCINERATION
LANDFILL
OCEAN DISPOSAL
RUNOFF
LEACHING
EVAPORATION
BIODEGRADATION
RUNOFF
LEACHING
EVAPORATION
BIODEGRADATION
ENVIRONMENT

Figure 1. Schematic representation of pesticide manufacturing plant emissions.

4.54×10^3 metric tons per year of most thioorganophosphate pesticides, for example, could emit over 907 metric tons per year of SO_2. Such a plant might also produce 2.27×10^3 metric tons to 4.54×10^3 metric tons per year of particulate pollutants, depending upon the fuel used for process heat and the air pollution controls installed.

Evaporation from holding ponds or evaporation lagoons may also be an emission source, although few quantitative data are available. Equations are presented which were used to predict the evaporation rates of several pesticides and develop evaporation emission factors for additional input into the prioritization model. These equations indicate that up to 5.6 kg/day of aldrin could be emitted from an evaporation lagoon having a surface area equal to 4.05×10^5 m^2 if aldrin were still manufactured.

Emissions, including particulates, gases, and vapors from the manufacturing process, emanate from various pieces of equipment (for example, reactors, driers, and condensers) and enter the atmosphere both as the active ingredient and as raw materials, intermediates, and byproducts. Air emission control devices used in the pesticide manufacturing industry include baghouses, cyclone separators, electrostatic precipitators, incinerators, and gas scrubbing units.

Major pesticide chemicals were rank ordered or prioritized based on their air pollution potential by computing a relative environmental impact factor. A prioritization was conducted because a realistic assessment of the environmental significance of air emissions from pesticide manufacturing plants is inconceivable due to the limited quantitative emissions data available. The prioritization model is simply one tool used to aid decision making regarding further characterization of the pesticide manufacturing industry. The pesticide ranking should by no means be considered rigid, but it should highlight areas for future consideration.

The prioritization list of 80 pesticides highlights two facts: 1) little information is available concerning the environmental burden due to potential evaporation emissions from holding ponds and evaporation lagoons, and 2) sulfur dioxide emissions may be substantial for some pesticides, resulting from flaring H_2S and mercaptans and the incineration of sulfur-containing compounds. Four of the nine pesticides receiving the highest prioritization impact factors are potentially emitted to the atmosphere from holding ponds or lagoons. Eight pesticides appear in the upper 20% of the prioritization list due primarily to the potentially high emission of SO_2, resulting from flaring H_2S and mercaptans and the incineration of sulfur-containing compounds.

Due to increasingly stringent regulations, rising costs, insect resistance to pesticide chemicals, and greatly increased reliance on herbicides for cultivation, changes are occurring in pest control strategies; however, chemical pesticides should continue to play a significant role in pest management. Pesticide production beyond the next few years is difficult to estimate because of diverse changes in government regulations, the influence of research on new products and on application rates of products, and a variety of economic factors. Production of synthetic organic pesticides is estimated to increase by an average of 1% annually until 1985 with average annual herbicide growth of approximately 2%, average annual insecticide growth unchanged from the present level, and average annual fungicide growth of approximately 1.8%. At this predicted growth rate, total synthetic organic pesticide production in 1985 will be 8.06×10^5 metric tons.

SECTION 3

PESTICIDE PRODUCTION

PRODUCTION STATISTICS

Pesticides have become an important factor in the United States economy because they are used to increase the production of food and fiber and to control organisms that destroy useful materials or threaten public health. A pesticide is defined as 1) any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest, or 2) any substance intended for use as a plant regulator, defoliant, or desiccant (1). Pesticides are usually classified by the kind of pest they control, purpose of application, or mode of action on a certain pest as listed in Table 1 (2).

TABLE 1. PESTICIDE CLASSES BY PURPOSE (2)

- Algicides
- Bacteriostats
- Defoliants
- Desiccants
- Fumigants
- Fungicides
- Growth regulants--insect and plant
- Herbicides
- Insecticides
- Larvacides
- Miticides (acaricides)
- Molluscicides
- Pheromones (attractants)
- Repellants
- Rodenticides
- Sterilants
- Synergists

The major pesticide classes in Table 1, based on the largest annual productions, are herbicides, insecticides, and fungicides. Herbicides are used for preventing or inhibiting the growth of plants or plant parts, or for killing or destroying them (3). Insecticides constitute a class of pesticide that prevents or inhibits the establishment, reproduction, development, growth or presence of any member of the class Insecta or other allied classes in the phylum Arthropoda considered to be pests (3). Fungicides are used on farm crops, preferably as protective rather than curative treatment, being applied to the surface of the plant in water suspensions or dusts before attack of a fungus (4).

---

(1) Pesticides and Pesticide Containers. Federal Register, 39(85):15236, 1974.

(2) Kelso, G. L., R. R. Wilkinson, and T. L. Ferguson. The Pollution Potential in Pesticide Manufacturing--1976 (Draft Final Report). Contract 68-02-1324, Task 43, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, April 16, 1976. 236 pp.

The 1974 production of all synthetic organic pesticides is estimated to have been 6.4 x 10^5 metric tons[a] (2). The 1974 production estimates were used as prioritization input, rather than more recent statistics, because these 1974 data are the only comprehensive data base for all pesticide categories as well as for individual pesticides. In order to provide a general overview of the industry, however, more recent production statistics are presented.

The 1975 production for all synthetic organic pesticides was 7.3 x 10^5 metric tons. Herbicides dominated the 1975 market, accounting for more than 48% of the total. Herbicide production in 1975 totaled 3.5 x 10^5 metric tons, a 30.4% increase over the previous year. Insecticide production in 1975 increased only 2.4%, reaching 3.0 x 10^5 metric tons or over 41% of the total synthetic organic pesticide production for that year. Production of fungicides in 1975, which accounted for less than 10% of the total, decreased 4.5% from the previous year to 7.1 x 10^4 metric tons (5).

Available statistics indicate that inorganic pesticides constitute only about 10% of the total U.S. pesticide production (5). Fungicides account for 55% of the inorganic pesticide business, herbicides for 38%, and insecticides for 7% (5). A total of 79 inorganic and metallic-organic pesticides were in use in 1973. Of these compounds, 28 were mercury based, 17 arsenic based, 11 copper based, 6 other metal based, and the remainder other inorganic compounds (6).

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[a] 1 metric ton equals 10^6 grams; conversion factors and metric system prefixes are presented at the end of this report (p. 138).

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(3) Ouellette, R. P., and J. A. King. Chemical Week Pesticides Register. McGraw-Hill Book Company, New York, New York, 1977. 346 pp.

(4) 1976 Farm Chemicals Handbook. Meister Publishing Co., Willoughby, Ohio, 1976. 577 pp.

(5) Ouellette, R. P., and J. A. King. Pesticides '76. Chemical Week, 118(25):27-38, 1976.

(6) Patterson, J. W. State-of-the-Art for the Inorganic Chemicals Industry: Inorganic Pesticides. EPA-600/2-74-009a, U.S. Environmental Protection Agency, Washington, D.C., March 1975. 39 pp.

Copper sulfate, zinc sulfate, sodium chlorate and sulfur are among the leading inorganic pesticides, but these compounds are primarily products of other industries and have other uses in addition to being pesticides. Sodium chlorate, for example, is used in the metallurgical, textile, dye, and pulp and paper industries, and as an agricultural herbicide, but the actual percentage of production used as a pesticide is not known. Inorganic pesticides were not included in the prioritization with the exception of arsenates, for which reasonably accurate estimates of pesticide use could be made. Also, the inclusion of inorganic arsenicals in the prioritization shows that their small production is a principal factor for their low ranking.

The pesticide market is dominated by a small number of major products, while a large number of minor products compete for a small share of the market. Thirty-seven major synthetic organic pesticides, those with production greater than or equal to 4,540 metric tons, accounted for 74% of the market in 1974. The remaining 26% of production was divided among about 300 other pesticides. A total of 140 to 150 synthetic organic pesticides are estimated to have had production greater than 454 metric tons in 1974 (2).

Actual production figures for specific pesticide compounds are usually not available unless there are three or more producers (none of which are excessively dominant over the others), because these data are considered proprietary by the companies and are accepted in confidence by the U.S. Tariff Commission. As a result of this reporting procedure, U.S. production data are not available on many pesticides, including the most widely used insecticide (toxaphene) and the largest selling herbicide (atrazine). Combined toxaphene and atrazine production accounts for an estimated 15% of all synthetic organic pesticide production in the United States (2).

U.S. production of synthetic organic pesticides in 1974 has been reported, by category, as shown in Table 2 (2). These basic data are utilized to develop production estimates for use in this study. Production estimates presented in Table 3 are believed to be accurate within ±10%. These estimates are based on the data in Table 2 as well as current knowledge regarding various segments of the pesticide industry gathered in part from confidential sources (2).

Table 4 presents estimated 1974 production of individual pesticides within each category (2).

TABLE 2. U.S. PRODUCTION OF SYNTHETIC ORGANIC PESTICIDES, BY USAGE CATEGORY, IN 1974 (2)

Pesticide usage categories	1974 Production,[a] 10^3 metric tons
Fungicides:	
Pentachlorophenol and sodium salts	23.8
Naphthenic acid, copper salt	0.9
Other cyclic fungicides	31.8
Dithiocarbamic acid salts	16.1
Other acyclic fungicides	1.3
Total fungicides	73.8
Herbicides and plant hormones:	
Maleic hydrazide	2.6
2,4-D acid,[b] dimethylamine salt	6.6
Other cyclic compounds	212.0
All acyclic compounds	52.8
Total herbicides and plant hormones	274.0
Insecticides, rodenticides, soil conditioners and fumigants:	
Aldrin-toxaphene group	64.3
Methyl parathion	23.3
Other cyclic organophosphorus insecticides	25.6
Methoxychlor	1.5
Other cyclic insecticides and rodenticides	72.8
Methyl bromide	13.8
Acyclic organophosphorus insecticides	35.7
Chloropicrin	2.2
Other acyclic insecticides, rodenticides, soil conditioners, and fumigants	55.8
Total	294.9
Total synthetic organic pesticide production, 1974	642.7

[a] Data may not add to totals due to independent rounding.

[b] 2,4-Dichlorophenoxyacetic acid.

TABLE 3. U.S. PRODUCTION OF SYNTHETIC ORGANIC PESTICIDES, BY CHEMICAL GROUPS, IN 1974 (2)

Chemical group	Estimated 1974 production,[a] 10^3 metric tons	Estimated percentage of total production (rounded)
Chlorinated hydrocarbons	208.6	33
Organophosphorus compounds	90.7	14
Carbamates	68.0	10
Triazines	68.0	10
Anilides	49.9	8
Other nitrogenous compounds	31.7	5
Organoarsenicals and organometallics	24.9	4
Diene-based compounds	18.1	3
Ureas and uracils	18.1	3
Nitrated hydrocarbons	18.1	3
All others	46.3	7
TOTAL	642.6	100

[a] Data may not add to totals due to independent rounding.

TABLE 4. ESTIMATED U.S. PRODUCTION OF MAJOR INDIVIDUAL SYNTHETIC ORGANIC PESTICIDES, BY CATEGORY, IN 1974 (2)

Chemical group	Pesticide	Estimated production,[a] 10^3 metric tons	Approximate percentage of group production
Chlorinated hydrocarbons	Toxaphene	49.9	24
	DDT[b]	27.2	13
	2,4-D acid, esters, salts	24.9	12
	PCP[c] and sodium salts	23.6	11
	Trichlorophenols	11.3	6
	Dichloropropene	11.3	6
	Chloramben	10.0	5
	DBCP[d]	9.1	4
	Sodium TCA[e]	6.8	3
	All others	34.5	16
		208.6	100
Organophosphates	Methyl parathion	23.1	25
	Malathion	13.6	15
	Parathion	7.7	9
	Diazinon	5.4	6
	Disulfoton	4.5	5
	Phorate	4.5	5
	Monocrotophos	3.2	4
	Fensulfothion	2.7	3
	Merphos	2.3	2
	All others	23.6	26
		90.7	100
Carbamates	Carbaryl	26.3	39
	Maneb	5.4	8
	Metalkamate	4.5	7
	Carbofuran	4.5	7
	Butylate	3.6	5
	Zineb	3.2	5
	EPTC[f]	2.7	4
	Nabam	2.3	3
	Vernolate	2.3	3
	Aldicarb	2.3	3
	All others	10.9	16
		68.0	100
Triazines	Atrazine	49.9	73
	Simazine	6.8	10
	Propazine	4.5	7
	All others	6.8	10
		68.0	100
Anilides	Propachlor	20.4	41
	Alachlor	18.1	36
	Propanil	6.8	14
	Butachlor	4.5	9
		49.9	100
Organoarsenicals and organometallics	MSMA[g]	15.9	64
	DSMA[h]	4.5	18
	Cacodylic acid	1.4	5
	Copper naphthenates	0.9	3
	All others	2.3	10
		24.9	100
Other nitrogenous compounds	Captan	9.1	29
	Methyomyl	4.5	14
	CDAA[i]	3.2	10
	Maleic hydrazide	2.7	9
	Benomyl	1.8	6
	Nitralin	1.4	4
	Picloram	1.4	4
	Captafol	1.4	4
	Folpet	1.4	4
	All others	5.0	16
		31.7	100
Diene-based	Chlordane	6.8	38
	Aldrin	4.5	25
	Endrin	1.4	7
	Heptachlor	1.4	7
	Endosulfan	1.4	7
	All others	2.7	16
		18.1	100
Ureas and uracils	Bromacil	5.4	30
	Diuron	4.5	25
	Fluometuron	2.3	13
	Linuron	1.4	7
	Terbacil	1.4	7
	All others	3.2	18
		18.1	100
Nitrated hydrocarbons	Trifluralin	11.3	63
	Chloropicrin	2.3	13
	Dinoseb	1.4	7
	Benefin	1.4	7
	All others	1.8	10
		18.1	100
All others	Methyl bromide	14.1	30
	Miscellaneous	32.2	70
		46.3	100
Total all synthetic organic pesticides		642.6	

[a] Data may not add to totals due to independent rounding.

[b] Dichlorodiphenyltrichloroethane.

[c] Pentachlorophenol.

[d] Also known as dibromochloropropane, the chemical name is 1,2-dibromo-3-chloropropane (principal constituent).

[e] Trichloroacetic acid.

[f] S-Ethyl n,n-dipropylthiocarbamate.

[g] Monosodium methanearsonate.

[h] Disodium methanearsonate.

[i] N,N-diallyl-2-chloroaceteamide.

PRODUCERS

In 1976, there were 139 pesticide manufacturing plants in the United States (excluding those that produce industrial chemicals with pesticide utility, which are mainly products of other industries), as shown in Figure 2 (2). These plants are distributed throughout 34 states, but major pesticide production plants, those with capacities over 2.27×10^3 metric tons, are located in 25 states. Table 5 (7) lists the 20 pesticide producing plants with the largest capacities. Many plants are located near the coast in close proximity to refineries that supply petroleum and chlor-alkali feedstocks. Approximately 25% of all the pesticide manufacturing plants are located in New Jersey and California, with 17% located in New Jersey alone. Pesticide plants vary in size from less than 2.27×10^4 kg/yr up to 9.07×10^4 metric tons/yr (7).

Approximately 60 plants produce only one active ingredient, and 86 plants (62% of the total) produce two or less. In contrast, however, several plants produce a large number of active ingredients, as shown in Table 6 (2, 7).

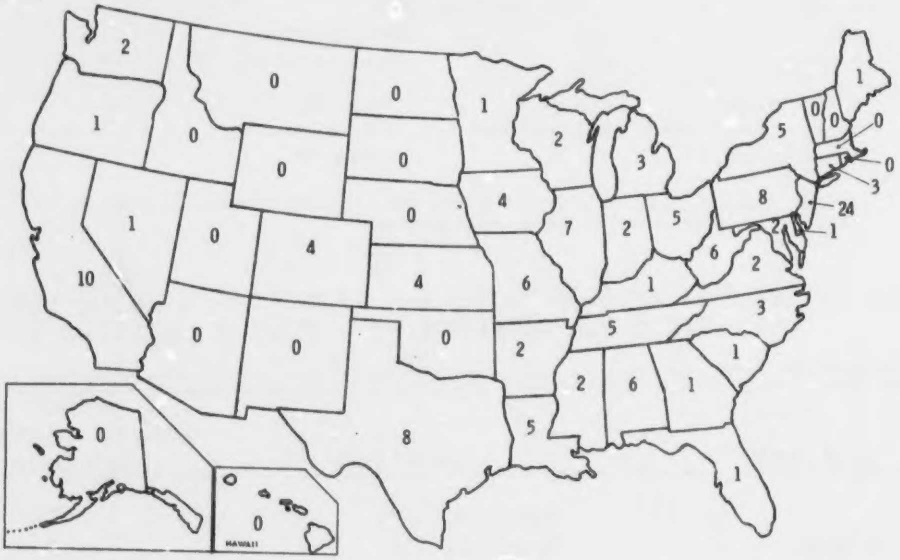

Figure 2. Pesticide production plant locations, by state, in 1976 (2).

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(7) Parsons, T. B. (ed.), and F. I. Honea. Industrial Process Profiles for Environmental Use: Chapter 8, Pesticides Industry. EPA-600/2-77-023h (PB 266 225), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, January 1977. 240 pp.

TABLE 5. SELECTED PESTICIDE PLANT LOCATIONS AND CAPACITIES IN 1972 (7)

Company	Major pesticide	Plant location	Estimated plant capacity, 10^3 metric tons
Ciba-Geigy Corporation	Atrazine	McIntosh, AL	90.7
	Diazinon	St. Gabriel, LA	6.8
Tenneco Chemical, Inc.	Toxaphene	Fords, NJ	56.7
Monsanto Chemicals	Alachlor	Muscatine, IA	13.6
	Maneb (dithiocarbamates)		6.8 to 9.1
	Pentachlorophenol	Sauget, IL	11.8
	Methyl parathion and parathion	Anniston, AL	22.7
Dow Chemical Company	2,4-D	Midland, MI	20.4 to 22.7
	Pentachlorophenol		8.2
	Dichlorobenzene		7.3
	Methyl bromide		6.8
Hercules, Inc.	Toxaphene	Brunswick, GA	22.7 to 34.0
Union Carbide Corporation	Carbaryl	Institute, WV	29.5
E. I. du Pont de Nemours and Company	Uracils (Bromacil)	LaPort, TX	9.1
	Ureas (Diuron)		13.6
Eli Lilly and Company	Trifluralin	Lafayette, IN	15.9
Velsicol	Chlordane	Marshall, IL	13.6
	Organophosphates	Bayport, TX	
American Cyanamid	Malathion	Warners, NJ	15.9
Stauffer Chemical Company	Parathion and methyl parathion	Mount Pleasant, TN	13.6
Ansul Company	MSMA	Marinette, WI	11.3
Diamond Shamrock Chemical Company	MSMA	Green Bayou, TX	9.1
Calhio Chemical	Captan	Perry, OH	11.3
Rohm and Haas Company	Dithiocarbamates	Philadelphia, PA	9.1 to 11.3
Shell Company Company[a]	Aldrin	Denver, CO	9.1

[a] Aldrin and dieldrin are no longer manufactured.

TABLE 6. PESTICIDE MANUFACTURERS PRODUCING A LARGE NUMBER OF ACTIVE INGREDIENTS AT A SINGLE LOCATION (2, 7)

Company	Location	Number of active ingredients produced
Dow	Midland, MI	28
Rorer-Amchem	Ambler, PA	22
Mobay	Kansas City, MO	21
Ciby-Geigy	St. Gabriel, LA	16
Transvaal	Jacksonville, AR	16
Blue Spruce	Edison, NJ	13
Rorer-Amchem	Fremont, CA	10
Riverdale	Chicago Heights, IL	10
McLaughlin Gormely King	Minneapolis, MN	10
Rorer-Amchem	St. Joseph, MO	10
FMC	Middleport, NY	10

The data in Tables 5 and 6 must be qualified to the extent that the plants either manufacture a given pesticide or have the capacity to manufacture a given pesticide. Pesticide producers generally do not simultaneously manufacture their entire product line but do have facilities for production of various pesticides without extensive plant modification.

PRODUCTION PROCESS

Technology for the production of pesticides varies considerably depending on the properties of the compounds. Generally, however, the pesticide industry employs unit operations and equipment similar to those used by the chemical processing industry (reaction kettles, driers, filters, etc.) (8). Two characteristics of the pesticide manufacturing industry differentiate it from many, if not all, of the large industries of environmental concern: 1) raw materials, byproducts, and products may be highly toxic to certain plants and animals (including man); and 2) the production processes normally require only low to moderate temperatures (2).

The raw materials required for pesticide production include many petroleum-based hydrocarbon chemicals from the petroleum and chemical industries, and some chlorine and sodium hydroxide from the chlor-alkali industry. Large amounts of sulfuric acid and nitric acid from the inorganic chemical industry are also used. Gases including chlorine, phosgene, and ammonia are used in the production of some pesticides, and these gases can be extremely toxic if released to the atmosphere. Atmospheric emissions of heavy metals, arsenic, cyanide, and phosphate raw materials, as well as partially chlorinated hydrocarbons, may also present a potential health hazard (7).

The raw material common to the most pesticides, elemental chlorine, is used directly on site in the production of chlordane, toxaphene, 2,4-D, 2,4,5-T, atrazine, captan, carbaryl, and mercuric chloride. Chlorine is also used to prepare raw materials brought in for the production of DDT, aldrin, and perhaps trifluralin and alachlor. Production of chlorine previously involved extensive use of mercury cells, leading to mercury losses, but these cells are being better controlled and are being displaced by mercury-free diaphragm cells. Unusually hazardous raw materials include hydrogen cyanide (of which over 4.54×10^3 metric tons are required annually for atrazine production), carbon disulfide, various amines, and concentrated acids and caustic. The P_2S_5 used in manufacturing organophosphorus pesticides, the C_5Cl_6 used for cyclodiene pesticides, the phosgene used to make carbaryl, and numerous other raw materials, as well as solvents, such as xylene, toluene, and similar materials, present potential health hazards (2).

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(8) Air Pollution Engineering Manual, Second Edition. J. A. Danielson, ed. Publication No. AP-40, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, May 1973. 987 pp.

Actual pesticide production processes require only low or moderate temperatures. Normally, these temperatures range from approximately 0°C to 200°C (personal communication with G. A. Richardson, Monsanto Research Corporation, 17 October 1977). The production of DDT, for example, is exothermic; the reactants are initially cooled to a temperature of 0°C to 30°C, and the cooling is continued to maintain the reaction temperature in this range (9). The batch preparation of DDT may be carried out at atmospheric pressure in a closed reaction vessel equipped with an agitator and a jacket, internal cooling coils, or an external heat exchanger circuit (9).

Plant equipment is generally newer for the more toxic materials such as the organophosphorus and carbamate insecticides which have undergone rapid growth in recent years. Many of the older chlorinated hydrocarbons and other products are manufactured in somewhat older equipment, up to and over 50 years old. The majority of basic facilities and equipment now in use for pesticide manufacture was designed and built prior to the present age of intense concern about the environment, and many manufacturers seem to be building or designing new pollution control equipment to bring their plants into conformity with local standards.

Equipment is usually isolated from other company activities, and it is dedicated to one pesticide or to two pesticides in the same chemical family with similar pesticidal applications. Cleanup of equipment is therefore minimized, and the associated pollution potential is not particularly significant. Only a small quantity of active ingredient (usually much less than 1% of equipment capacity) is involved in this operation, and the wastes generated are usually recycled, discharged to the plant waste treatment system, or combusted as fuel (2).

Information regarding the energy requirements for the pesticide industry is generally not available since many of the production processes are proprietary. The feedstock raw materials such as chlorine and sodium hydroxide may require large amounts of energy if electrodialysis of a brine solution is used, but most of these feedstocks are actually products of the chlor-alkali, petroleum, and chemical industries. The final pesticide reactions themselves require relatively low amounts of energy for heating and maintaining reaction temperatures, for some reflux and stripping operations, and for pumping fluids (7).

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(9) Sittig, M. Agricultural Chemicals Manufacture - 1971. Noyes Data Corporation, Park Ridge, New Jersey, 1971. 264 pp.

SECTION 4

INDUSTRY SEGMENTATION

A variety of manufacturing processes are utilized in the pesticide industry due to the large number of chemical compounds used as pesticides. The Federal Register has published a comprehensive list of 1,605 pesticide active ingredients for reregistration (10). Over 300 pesticide products are in current production and use, and over 500 pesticide products have been identified (2, 7). The pesticide industry is therefore difficult to categorize in terms of processes and operations. In this respect, it is not like other portions of the chemical industry. The bromine industry, for example, is concentrated in Arkansas and Michigan and is dominated by six producers and essentially one process. Similarly, the vinyl chloride industry is composed of 11 companies located at 15 sites and utilizing 4 different manufacturing processes. It is possible to describe the vinyl chloride manufacturing operation in terms of a representative facility having measured and/or estimated emission rates. The chemistry of the emitted pollutants from a vinyl chloride plant is well known, and emission standards in terms of threshold limit values (TLV®) have been established for these pollutants. The pesticide industry cannot be similarly categorized, nor have emission standards been established for many pollutants from this industry (2).

In order to present a clearer picture of the process relationships in the pesticide industry, the pesticides have been separated, based on similarities in chemical structures and synthesis reactions, into 12 industrial segments (7). Based on production estimates from Table 4 the following segments are arranged in decreasing order:

- simple and aromatic chlorinated hydrocarbon pesticides
- organophosphate pesticides
- carbamate pesticides
- triazine pesticides
- anilide pesticides
- organoarsenic and organometallic pesticides
- other nitrogenous pesticides

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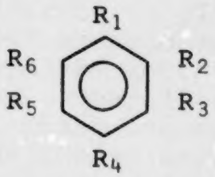
(10) Pesticide Programs: Data Requirements to Support Registration of Pesticide Active Ingredients and Preliminary Schedule for Call-Ins. Federal Register, 41(32):7218-7376, 1976.

- diene-based chlorinated pesticides
- urea and uracil pesticides
- nitrated hydrocarbon pesticides
- microbial and naturally-occurring pesticides
- other pesticides

Many of the production processes in the industry are considered proprietary, and detailed operational data and process descriptions are of limited availability. In addition, some pesticides may be produced by as many as eight different processes, none specifically identified with a particular producer or plant (7). Due to the limited availability of detailed data and the variety of potential production processes, the following descriptions of the 12 industrial sements are somewhat generalized.

SIMPLE AND AROMATIC CHLORINATED HYDROCARBON PESTICIDES

The simple and aromatic chlorinated hydrocarbon pesticides include about 90 pesticides which may be separated into three groups: 1) simple chlorinated hydrocarbons, 2) DDT-family of chlorinated hydrocarbons, and 3) aromatic-chlorinated hydrocarbons. Pesticides having phenol as a base ("phenoxie" pesticides) are included as aromatic-chlorinated hydrocarbons. The general structure of aromatic-chlorinated hydrocarbons is (7):



where at least one R group is chlorine, as summarized in the following tabulation (7).

Aromatic pesticide	R_1	R_2	R_3	R_4	R_5	R_6
Phenoxie pesticides						
2,4-D	$-OCH_2COOH$	-Cl	-H	-Cl	-H	-H
2,4-DB[a]	$-OCH_2CH_2COOH$	-Cl	-H	-Cl	-H	-H
MCPA[b]	$-OCH_2COOH$	$-CH_3$	-H	-Cl	-H	-H
MCPB[c]	$-CH_2CH_2COOH$	$-CH_3$	-H	-Cl	-H	-H
2,4,5-T[d]	$-OCH_2COOH$	-Cl	-H	-Cl	-Cl	-H
Silvex	$-OCH(CH_3)COOH$	-Cl	-H	-Cl	-Cl	-H
Bromoxynil	-CN	-H	-Br	-OH	-Br	-H
PCP	-OH	-Cl	-Cl	-Cl	-Cl	-Cl
2,4,5-Trichlorophenol	-OH	-Cl	-H	-Cl	-Cl	-H

---

[a] 4-Chloro-2-oxobenzothiazolin-3-ylacetic acid (benazolin).

[b] [(4-Chloro-*o*-tolyl)oxy]acetic acid.

[c] 4-[(4-Chloro-*o*-tolyl)oxy]butyric acid.

[d] (2,4,5-Trichlorophenoxy)acetic acid.

Aromatic pesticide (continued)	R_1	R_2	R_3	R_4	R_5	R_6
Others						
PCNB[e]	$-NO_2$	-Cl	-Cl	-Cl	-Cl	-Cl
2,3,6-TBA[f]	-COOH	-Cl	-H	-Cl	-H	-Cl
Chloramben	-COOH	-H	-Cl	-H	$-NH_2$	-Cl
Dichlorobenzene	-Cl	-H	-H	-Cl	-H	-H
Hexachlorobenzene	-Cl	-Cl	-Cl	-Cl	-Cl	-Cl
Dicamba	-COOH	$-OCH_3$	-Cl	-H	-H	-Cl

---

[e] Pentachloronitrobenzene.

[f] Trichlorobenzoic acid.

The estimated annual production of chlorinated hydrocarbon pesticides in 1974 was 208.6×10^3 metric tons. Toxaphene, the most extensively used insecticide in the United States, accounted for 24% of this total. DDT production, accounting for 13% of the total, was estimated as 27.2×10^3 metric tons in 1974. Phenoxie pesticides are used as herbicides, and 2,4-D acid, esters, and salts accounted for 24.9×10^3 metric tons in 1974 (2). A number of chlorinated hydrocarbon pesticides, such as DDT and 2,4,5-T have been banned from U.S. distribution, have had U.S. registrations canceled, or are under review due to their potential carcinogenicity. Twenty-four substitute pesticides have been nominated to replace DDT as discussed in Section 7. Several uses of the herbicide 2,4,5-T have been restricted, and eight herbicides (bromacil, MSMA/DSMA, cacodylic acid, dinoseb, dicamba, monuron, simazine, and trifluralin) have been nominated as replacements (5). Methyl bromide is included in this industry segment based on similarities with chlorinated hydrocarbon pesticides.

Chemical reactions involved in the synthesis of various chlorinated hydrocarbon pesticides are presented in Figure 3. Table 7 shows the raw materials used in production of several chlorinated hydrocarbon pesticides.

ORGANOPHOSPHATE PESTICIDES

Organophosphate pesticides, most of which are insecticides, are hydrocarbon compounds containing one or more phosphorus atoms. The organophosphates may be separated into three main groups: 1) those derived from phosphorus pentasulfide (P_2S_5), 2) those derived from thiophosphoryl chloride ($PSCl_3$), and 3) those derived from phosphorus trichloride (PCl_3). The typical structure of acyclic organophosphorus pesticides (those derived from P_2S_5 or $PSCl_3$) and a tabular presentation of several pesticides are shown in Table 8. Table 9 presents the typical structure and several examples of cyclic organophosphate pesticides (those derived from PCl_3) (7).

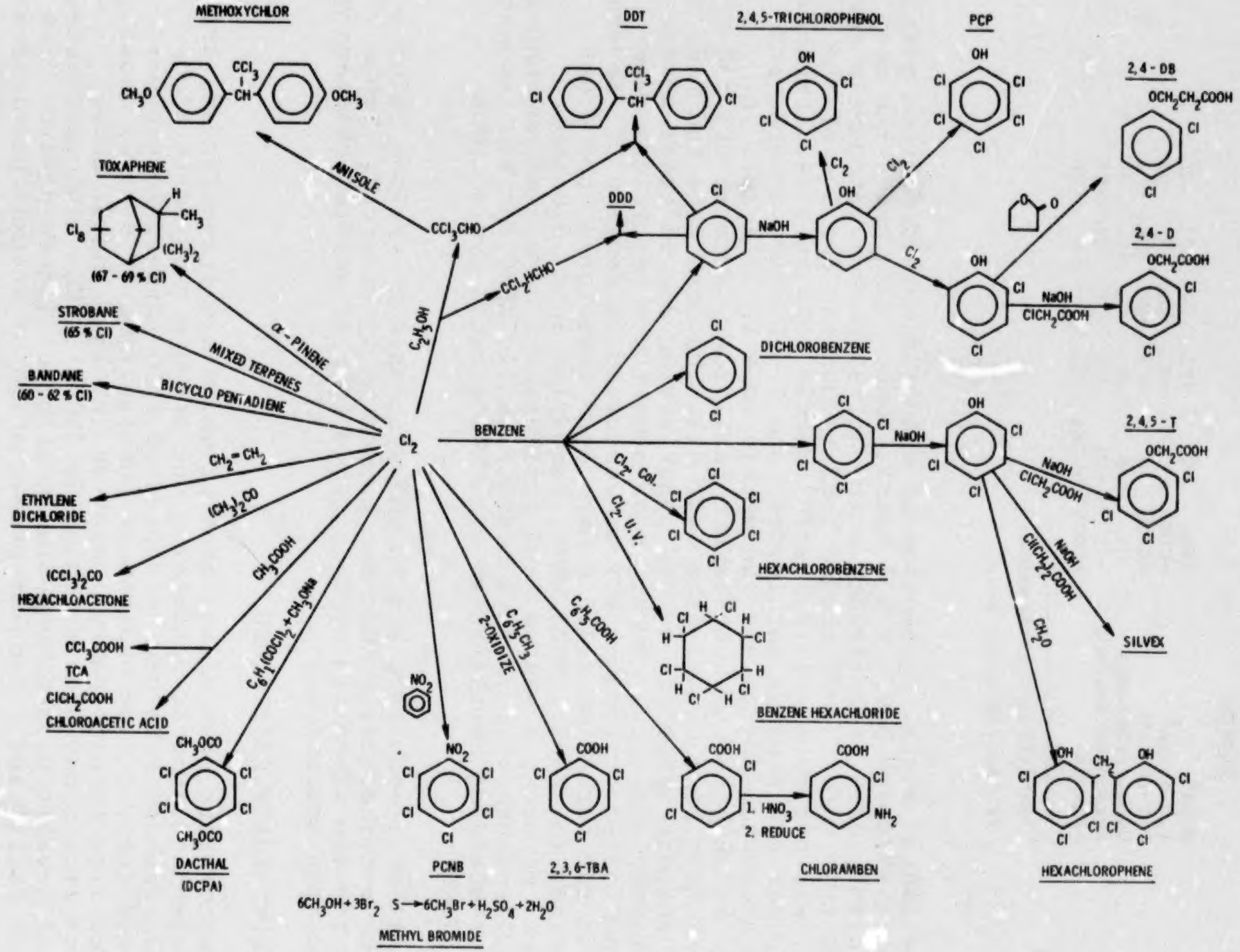

METHOXYCHLOR
DDT
2,4,5-TRICHLOROPHENOL
PCP
2,4-DB
TOXAPHENE
(67 - 69 % Cl)
ANISOLE
CCl_3CHO
DDD
CCl_2HCHO
C_2H_5OH
NaOH
Cl_2
2,4-D
NaOH
$ClCH_2COOH$
STROBANE
(65 % Cl)
α-PINENE
MIXED TERPENES
BANDANE
(60 - 62 % Cl)
BICYCLO PENTADIENE
DICHLOROBENZENE
Cl_2
BENZENE
2,4,5-T
$CH_2=CH_2$
ETHYLENE DICHLORIDE
$(CH_3)_2CO$
Cl_2, Cat.
Cl_2, U.V.
HEXACHLOROBENZENE
$(CCl_3)_2CO$
HEXACHLOACETONE
CH_3COOH
C_6H_5COOH
$CHCH_3COOH$
SILVEX
CH_2O
CCl_3COOH
TCA
$ClCH_2COOH$
CHLOROACETIC ACID
$C_6H_4(COCl)_2 + CH_3ONa$
$C_6H_5CH_3$
2-OXIDIZE
BENZENE HEXACHLORIDE
1. HNO_3
2. REDUCE
DACTHAL
(DCPA)
PCNB
2,3,6-TBA
CHLORAMBEN
HEXACHLOROPHENE
$6CH_3OH + 3Br_2 \quad S \rightarrow 6CH_3Br + H_2SO_4 + 2H_2O$
METHYL BROMIDE

Figure 3. Synthesis of some chlorinated hydrocarbons and related pesticides (7).

TABLE 7. INPUT MATERIALS FOR CHLORINATED HYDROCARBON PESTICIDES (7)

Pesticide	Input materials
Toxaphene	Chlorine, α-pinene
Strobane	Chlorine, mixed terpenes
Bandane	Chlorine, bicyclopentadiene
Ethylene dichloride	Chlorine, ethylene
Hexachloracetone	Chlorine, acetone
Chloroacetic acid	Chlorine, acetic acid
TCA	Chlorine, acetic acid (3 moles)
Dalapon	Chlorine, propionic acid
PCNB	Chlorine, nitrobenzene
Dacthal (DCPA)	Chlorine, $C_6H_4(COCl)_2$, CH_3ONa
Dicamba	Chlorine, benzene, methanol, CO_2, $(CH_3)_2SO_4$
2,3,6-TBA	Chlorine, toluene, oxygen
Chloramben	Chlorine, benzoic acid, ammonia
Methoxychlor	Chlorine, ethanol, anisole
DDD[a]	Chlorine, ethanol, chlorobenzene
DDT	Chlorine, ethanol, chlorobenzene
2,4,5-Trichlorophenol	Phenol, chlorine
PCP	Phenol, chlorine
2,4-D	2,4-Dichlorophenol, $ClCH_2COOH$, NaOH
2,4-DB	2,4-Dichlorophenol, butyrolacetone
Dichlorobenzene	Chlorine, benzene
Hexachlorophene	2,4,5-Trichlorophenol, CH_2O
2,4,5-T	2,4,5-Trichlorophenol, NaOH, $ClCH_2COOH$
Silvex	2,4,5-Trichlorophenol, NaOH, $Cl(CH_2)_2COOH$
Hexachlorobenzene	Chlorine, benzene, catalyst
Benzene hexachloride	Chlorine, benzene, UV light source
MCPA	4-Chloro-*o*-cresol, sodium monochloroacetate
MCPB	4-Chloro-*o*-cresol, butyrolactone
Bromoxynil[b]	4-Hydroxybenzaldehyde, bromine, (NH_2OH)
Dichloropropene	1,3-Dichloro-2-propanol, $POCl_3$
Methyl bromide[c]	Methyl alcohol, bromine, and sulfur (Alternate: methyl alcohol and hydrobromic acid)

---

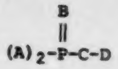
[a] 2,2-Bis(*p*-chlorophenyl)-1,1-dichloroethane (common name - TDE).

[b] Bromoxynil is classified as a phenoxie but is brominated instead of chlorinated.

[c] Methyl bromide is included in this industry segment based on similarities with chlorinated hydrocarbon pesticides.

TABLE 8. CHEMICAL STRUCTURE OF ACYCLIC ORGANOPHOSPHATE PESTICIDES (7)

Monophosphorus:



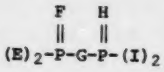
$$(A)_2-\overset{\overset{B}{\|}}{P}-C-D$$

Me = methyl

Et = ethyl

	A	B	C	D
(Systox) Demeton (mixture)	EtO	S	O	$CH_2CH_2SC_2H_5$
	EtO	O	S	$CH_2CH_2SC_2H_5$
Dichlorvos	MeO	O	O	$CH = CCl_2$
Dicrotophos	MeO	O	O	$C(CH_3) = CHCON(CH_3)_2$
Dimethoate	MeO	S	S	$CH_2CONHCH_3$
Disulfoton	EtO	S	S	$CH_2CH_2SC_2H_5$
Malathion	MeO	S	S	$CHCOOC_2H_5$ $CH_2COOC_2H_5$
Mevinphos	MeO	O	O	$C(CH_3) = CHCON(CH_3)_2$
Monitor	Meo and MeS	O	-	NH_2
Monocrotophos	MeO	O	O	$C(CH_3) = CHCONHCH_3$
Naled	MeO	O	O	$CHBrCBrCl_2$
Oxydemeton-methyl (mixture) (*m*-systox)	MeO	S	O	$CH_2CH_2SC_2H_5$
	MeO	O	S	$CH_2CH_2SC_2H_5$
Phorate (Thimet)	EtO	S	S	$CH_2SC_2H_5$
Phosphamidon	MeO	O	O	$C(CH_3) = CClCON(C_2H_5)_2$
Trichlorfon	MeO	O	-	$CH(OH)CCl_3$

Diphosphorus:



$$(E)_2-\overset{\overset{F}{\|}}{P}-G-\overset{\overset{H}{\|}}{P}-(I)_2$$

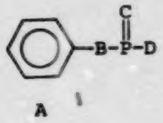
	E	F	G	H	I
Aspon	C_3H_7O	S	O	S	C_3H_7O
Ethion	EtO	S	SCH_2S	S	EtO
TEPP[a]	EtO	O	O	O	EtO

---

[a] Tetraethyl pyrophosphate.

TABLE 9. CHEMICAL STRUCTURE OF CYCLIC ORGANOPHOSPHATE PESTICIDES (7)

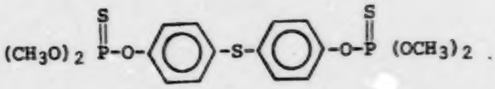
Substituted phenyls:



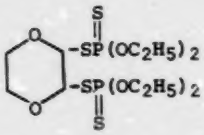
Pesticide	A	B	C	D
Carbophenothion	4-chlorophenyl	SCH_2S	S	$(OC_2H_5)_2$
Crotoxyphos	Phenyl	$(CH_3)CHOCCH = C(CH_3)O$	O	$(OCH_3)_2$
Crufomate	4-*t*-butyl-2-chlorophenyl	O	O	(1) OCH_3 (1) $NHCH_3$
Dyfonate (fonofos)	Phenyl	S	S	(1) OC_2H_5 (1) C_2H_5
Fensulfotion (Dasanit)	4-(methylsulfinyl)pheny	O	S	$(OC_2H_5)_2$
Fenthion	4-methylthio-*m*-cresol	O	S	$(OCH_3)_2$
Methyl parathion	4-nitrophenyl	O	S	$O(CH_3)_2$
Parathion	4-nitrophenyl	O	S	$O(C_2H_5)_2$
Fenchlorphos (Ronnel)	2,4,5-trichlorophenyl	O	S	$(OCH_3)_2$
Dicapthon	2-chloro-4-nitrophenyl	O	S	$(OCH_3)_2$
Famophos	N,N-dimethyl-phenyl-4-sulfonamide	O	S	$(OCH_3)_2$

Two diphosphorus compounds:

Abate

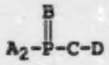


Dioxathion

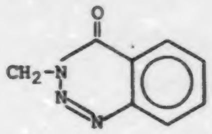
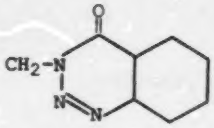
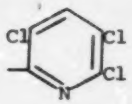
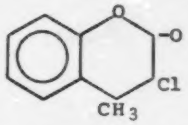
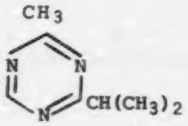
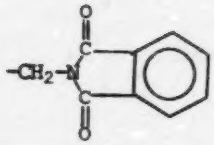


(continued)

TABLE 9 (continued)

Other cyclic structure: 

$A_2-\overset{B}{\overset{\|}{P}}-C-D$

	A	B	C	D
Azinphos-methyl (Guthion)	CH_3O	S	S	
Azinphos-ethyl	C_2H_5O	S	S	
Dursban	C_2H_5O	S	O	
Coumaphos	C_2H_5O	S	O	
Diazinon	C_2H_5O	S	O	
Phosmet (Imidan)	CH_3O	S	S	

The development of organophosphorus insecticides was an outgrowth of World War II research on organophosphorus compounds used as nerve gas. Tetraethyl pyrophosphate (TEPP) was the first commercial insecticide of this industry segment, followed by parathion and methyl parathion in the late 1940's. Methyl parathion, an acyclic organophosphate, is currently the nation's most widely used organophosphorus insecticide with an estimated annual production of 23.1×10^3 metric tons (2).

More than 100,000 organophosphorus compounds have been screened as possible insecticides (11). Among the most widely used today, besides methyl parathion and parathion, are malathion, diazinon, disulfoton, chlorpyriphos, phorate, fonofos, azinophos-methyl (Guthion), dimethoate, monocrotophos, and methidathion.

The organophosphorus insecticides kill insects by inactivating cholinesterase and acetylcholinesterase, which are found in nerve cells and the brain and play a vital role in nerve action. These compounds break down more rapidly to form innocuous substances in plants, animals, and the soil than do the chlorinated hydrocarbon pesticides. Organophosphorus insecticides do not accumulate in animals to produce harmful effects. Therefore, some can be used to protect crops shortly before harvest without leaving potentially harmful residues. The organophosphorus insecticides are usually active against a narrower range of insects than are the organochlorines. They are, however, more expensive than organochlorines and, since they degrade more rapidly, they generally must be applied more often to crops. Because they are usually more toxic to humans, they must be handled with greater care (11).

A number of organophosphates, such as phorate, disulfoton, dimethoate, monocrotophos, dicrotophos, demeton, and mevinphos, act as systemic insecticides, meaning that when sprayed on plants they do not remain on the surface but are rapidly translocated to many parts of it. Thus, plants do not have to be resprayed frequently to protect areas of new growth, and less of the insecticide is lost to rain or spray irrigation. However, when systemic compounds are applied to food crops, care must be taken so that excessive residues are not present in edible parts of the plant when harvested (11).

Chemical reactions and their relationships for key pesticides in the three main organophosphate groups are presented in Figures 4, 5, and 6. The input materials used in the manufacture of these pesticides are shown in Table 10.

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(11) Sanders, H. J. New Weapons Against Insects. Chemical and Engineering News, 53(30):18-31, 1975.

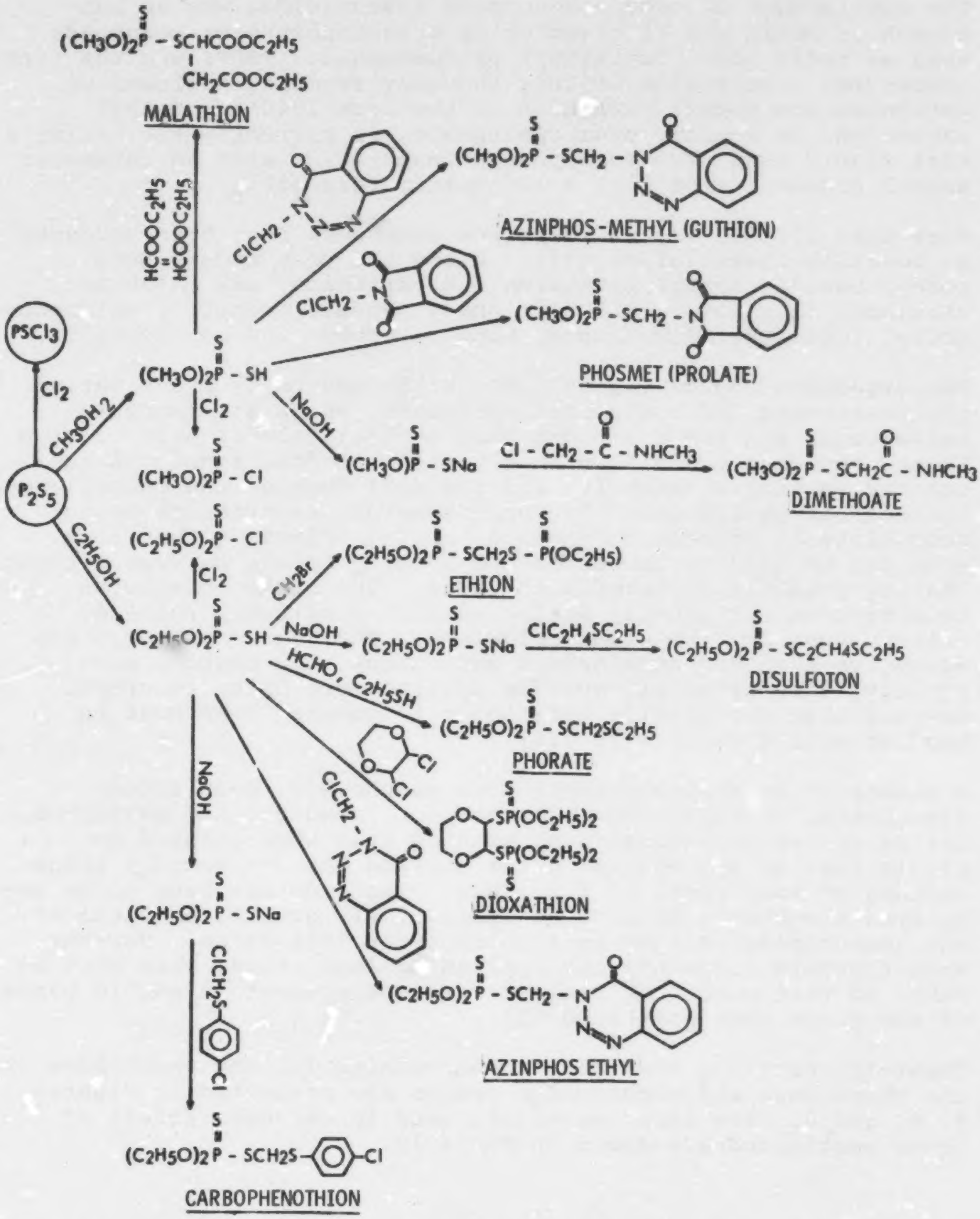
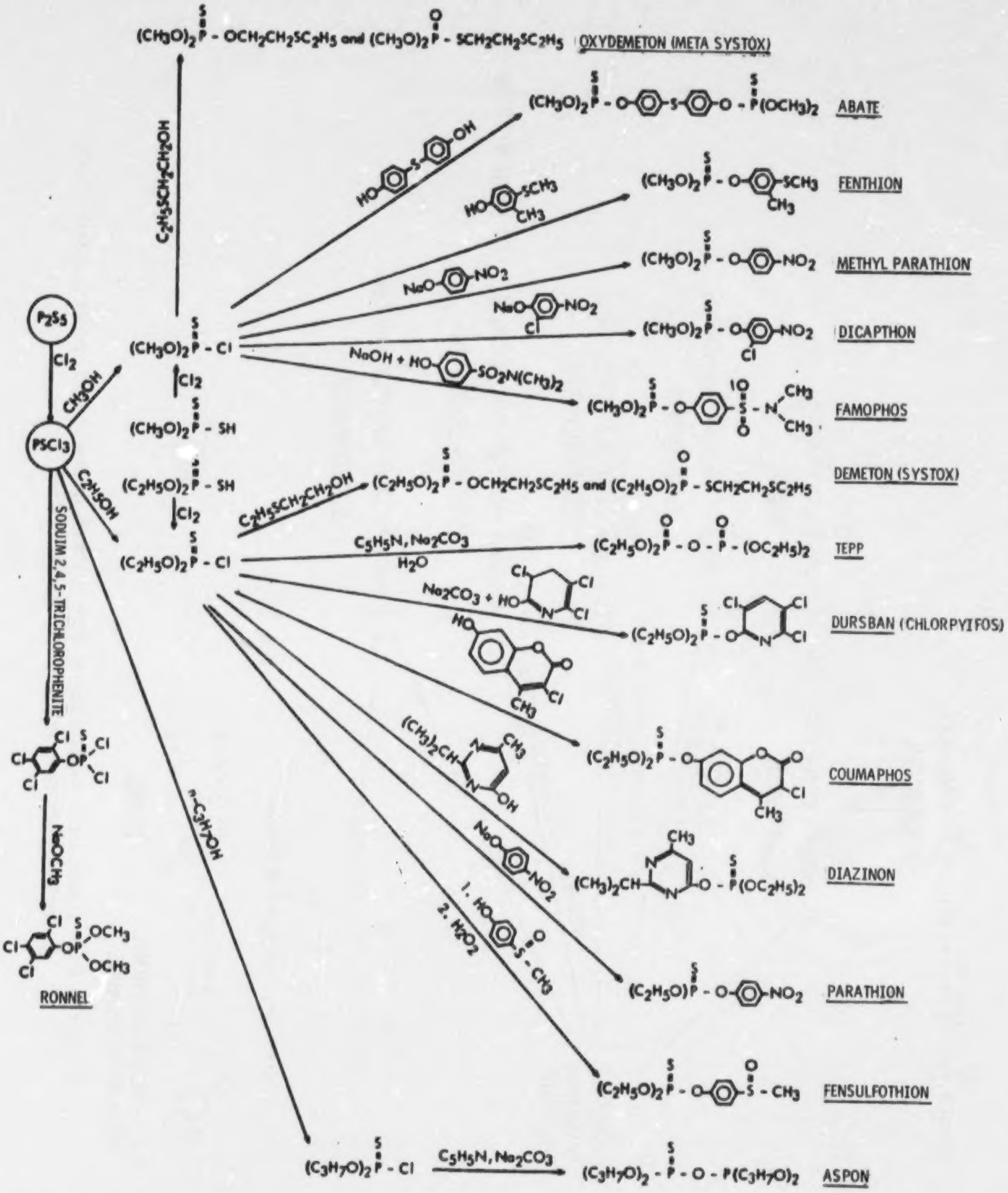

(CH3O)2P(S) - SCHCOOC2H5
CH2COOC2H5
MALATHION
HCOOC2H5
HCOOC2H5
ClCH2 - N
(CH3O)2P(S) - SCH2 - N
AZINPHOS-METHYL (GUTHION)
ClCH2 - N
(CH3O)2P(S) - SCH2 - N
PHOSMET (PROLATE)
PSCl3
Cl2
P2S5
CH3OH 2
(CH3O)2P(S) - SH
Cl2
(CH3O)2P(S) - Cl
NaOH
(CH3O)P(S) - SNa
Cl - CH2 - C(O) - NHCH3
(CH3O)2P(S) - SCH2C(O) - NHCH3
DIMETHOATE
C2H5OH
(C2H5O)2P(S) - Cl
Cl2
(C2H5O)2P(S) - SH
CH2Br
(C2H5O)2P(S) - SCH2S - P(S)(OC2H5)
ETHION
NaOH
(C2H5O)2P(S) - SNa
ClC2H4SC2H5
(C2H5O)2P(S) - SC2CH4SC2H5
DISULFOTON
HCHO, C2H5SH
(C2H5O)2P(S) - SCH2SC2H5
PHORATE
Cl
Cl
SP(OC2H5)2
SP(OC2H5)2
DIOXATHION
ClCH2 - N
NaOH
(C2H5O)2P(S) - SNa
ClCH2S - Cl
(C2H5O)2P(S) - SCH2 - N
AZINPHOS ETHYL
(C2H5O)2P(S) - SCH2S - Cl
CARBOPHENOTHION

Figure 4. Chemical reactions for organophosphate pesticides from phosphorus pentasulfide (7).



P2S5
Cl2
PSCl3
CH3OH
C2H5OH
SODIUM 2,4,5-TRICHLOROPHENITE
NaOCH3
n-C3H7OH
C2H5SCH2CH2OH
C5H5N, Na2CO3
H2O
Na2CO3 + HO
NaOH + HO
1. HO
2. H2O2
OXYDEMETON (META SYSTOX)
ABATE
FENTHION
METHYL PARATHION
DICAPTHON
FAMOPHOS
DEMETON (SYSTOX)
TEPP
DURSBAN (CHLORPYIFOS)
COUMAPHOS
DIAZINON
PARATHION
FENSULFOTHION
ASPON
RONNEL

Figure 5. Chemical reactions for organophosphate pesticides from phosphorus trichlorosulfide (7).

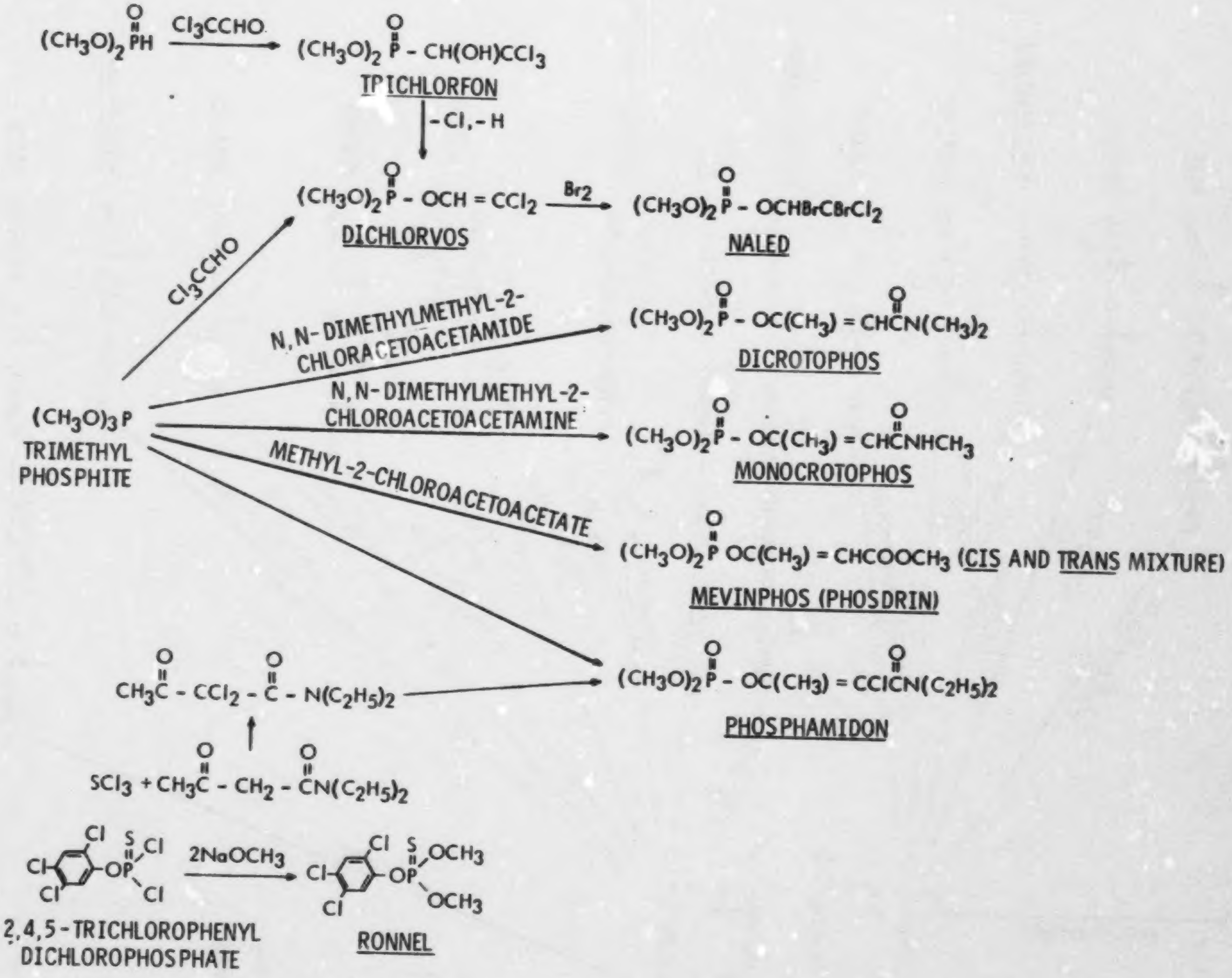

(CH3O)2PH
Cl3CCHO
(CH3O)2 P - CH(OH)CCl3
TRICHLORFON
-Cl, -H
(CH3O)2 P - OCH = CCl2
Br2
(CH3O)2 P - OCHBrCBrCl2
DICHLORVOS
NALED
Cl3CCHO
N, N-DIMETHYLMETHYL-2-CHLORACETOACETAMIDE
(CH3O)2 P - OC(CH3) = CHCN(CH3)2
DICROTOPHOS
N, N-DIMETHYLMETHYL-2-CHLOROACETOACETAMINE
(CH3O)3 P
TRIMETHYL PHOSPHITE
(CH3O)2 P - OC(CH3) = CHCNHCH3
MONOCROTOPHOS
METHYL-2-CHLOROACETOACETATE
(CH3O)2 P OC(CH3) = CHCOOCH3 (CIS AND TRANS MIXTURE)
MEVINPHOS (PHOSDRIN)
CH3C - CCl2 - C - N(C2H5)2
(CH3O)2 P - OC(CH3) = CClCN(C2H5)2
PHOSPHAMIDON
SCl3 + CH3C - CH2 - CN(C2H5)2
2NaOCH3
2,4,5-TRICHLOROPHENYL DICHLOROPHOSPHATE
RONNEL

Figure 6. Chemical reactions for organophosphate pesticides from other phosphorus compounds (7).

TABLE 10. INPUT MATERIALS FOR ORGANOPHOSPHATE PESTICIDES

Pesticide	Input materials
Acyclic:	
Aspon	*O*-*O*-Di-*n*-propyl phosphorochloridothioate, water, pyridine and sodium carbonate
DEF[a]	Butyl mercaptan and phosphorus oxychloride
Demeton	*O*-*O*-Diethyl phosphorochloridothioate and 2-hydroxethyl ethyl sulfide
Dichlorvos	Trimethyl phosphite and chloral (Alternate: triclorfon)
Dicrotophos	Trimethyl phosphite and N,N-dimethyl methyl-2-chloroacetoacetamide
Dimethoate	Sodium dimethylphosphorodithioate and N-methyl-*a*-chloroacetamide
Disulfoton	Sodium diethylphosphorodithioate and *B*-chloroethyl thioethyl ether
Ethion	*O*-*O*-Diethyl phosphorodithioic acid and dibromomethane
Malathion	*O*-*O*-Dimethyl phosphorodithioic acid and diethyl maleate
Merphos	Butyl mercaptan and phosphorus trichloride (Alternate: dibutyldisulfide and phosphorus)
Mevinphos	Trimethyl phosphate and methyl-2-chloroacetoacetate
Monitor	*O*-*O*-Dimethylphosphoroamidothioate
Monocrotophos	Trimethyl phosphite and N-methyl methyl-2-chloro-acetoacetamine
Naled	Dichlorvos and bromine
Methyl demeton (oxydemeton)	Dimethyl phosphorochloridothioate and 2-hydroxyethyl ethyl sulfide
Phorate	*O*-*O*-Diethyl phosphorodithioic acid, formaldehyde and ethyl mercaptan
TEPP	Diethyl phosphorochloridothioate and water (with pyridine and sodium carbanate)
Phosphamidon	Trimethyl phosphite, sulfurylchloride and acetoacetic acid diethylamide
Trichlorfon	Dimethyl phosphite and chloral

(continued)

TABLE 10 (continued).

Pesticide	Input materials
Cyclic:	
Abate	Dimethyl phosphorochloridothionate and bis-(P-hydroxyphenyl) sulfide
Azinphos-methyl (Guthion)	*o-o*-Dimethyl phosphorodithioic acid and N-chloromethylbenzazimide
Carbophenothion	*o-o*-Diethyl phosphorodithioic acid and N-chloromethylbenzazimide
Dursban (clopyrifos)	Sodium diethylphosphorodithioate and 4-chlorophenyl chloromethyl sulfide
Crotoxyphos	Diethyl phosphorochloridothioate and 3,5,6-trichloro-2-pyridinol
Coumaphos	Diethyl phosphorochloridothionate and 3-chloro-4-methyl-7-hydroxycoumarin
Crufomate	4-*t*-Butyl-2-chlorophenol, phosphonyl chloride, methanol, methylamine
Diazinon	Diethyl phosphorochloridothionate and 2-isopropyl-4-methyl-6-hydroxyprimidine
Dioxathion	*o-o*-Diethyl phosphorodithioic acid and 2,3-dichloro-*p*-dioxane
Dyfonate (fonophos)	No data
Dasanit (fensulfothion)	Diethyl phosphorochloridothioate and 4-methylthio-1-hydroxybenzene
Fenthion	Dimethyl phosphorochloridothionate and 4-methyl-thio-*m*-cresol
Methyl parathion	Dimethyl phosphorochloridothioate and sodium 4-nitrophenate
Parathion	Diethyl phosphorochloridothioate and sodium 4-nitrophenate
Phosmet (Imidan)	Sodium dimethylphosphorodithioate phthalimide, formaldehyde and chlorine
Fenchlorophos (Ronnel)	2,4,5-Trichlorophenyl phosphorochloridothioate sodium and methanol
Dicupthon	Dimethyl phosphorochloridothionate and sodium 2-chloro-4-nitrophenate
Famophos	*o-o*-Dimethyl phosphorochloridothioate, N,N-dimethyl-1-phenol-sulfonomide, sodium hydroxide and water

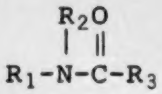
---

[a] S,S,S-Tributylphosphorotrithioate.

CARBAMATE PESTICIDES

Carbamate pesticides have the characteristic carbamate carbon-nitrogen (-N-C-) structure. There are more than 50 of these, which may be separated into three groups: 1) carbamate pesticides, 2) thiocarbamate pesticides, and 3) dithiocarbamate acid salt pesticides.

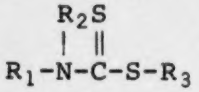
The structure of the major carbamate and thiocarbamate pesticides is:



$$R_1\text{-}\overset{\overset{\displaystyle R_2}{|}}{N}\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}R_3$$

as summarized in Table 11 (7).

The dithiocarbamate acid salts have the characteristic carbamate structure with two sulfur atoms added[a]:



$$R_1\text{-}\overset{\overset{\displaystyle R_2}{|}}{N}\text{-}\overset{\overset{\displaystyle S}{\|}}{C}\text{-}S\text{-}R_3$$

The structures of dithiocarbamate acid salt pesticides are summarized below.

Pesticide	R_1	R_2	R_3
CDEC[b]	$-C_2H_5$	$-C_2H_5$	$-CH_2CCl{=}CH_2$
Dimethyl dithiocarbamic acid, K salt	$-CH_3$	$-CH_3$	-K
Dimethyl dithiocarbamic acid, Mn salt	$-CH_3$	$-CH_3$	=Mn
Ethylene bis(dithiocarbamic acid), ammonia salt	$=C_2H_4$	-H	$-NH_4$
Ferbam	$-CH_3$	$-CH_3$	$={}^1/_3$ Fe
Maneb	$=C_2H_4$	-H	=Mn
Metham-sodium	$-CH_3$	-H	-Na
Nabam	$=C_2H_4$	-H	-Na
Zineb	$=C_2H_4$	-H	=Zn

The first commercial carbamate insecticide to be used on a large scale in the United States was carbaryl, introduced by Union Carbide in 1958 (11). Accounting for approximately 38% of this group's annual production, carbaryl is used widely today to control insects on cotton, vegetables, fruits, rice, sugarcane and ornamental plants.

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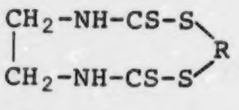
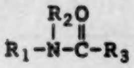
[a] For maneb, nabam, and zineb the structure is better represented as:



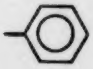
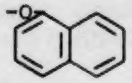
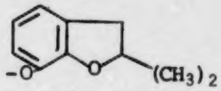
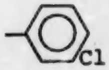
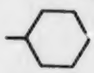
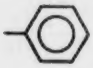
where R indicates the corresponding metals.

[b] 2-Chloroallyl-N,N-diethyldithiocarbamate (Vegadex®).

TABLE 11. STRUCTURE OF CARBAMATE AND THIOCARBAMATE PESTICIDES (7)



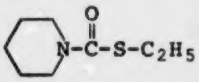
$$R_1-\overset{\displaystyle R_2}{\overset{|}{N}}-\overset{\displaystyle O}{\overset{\|}{C}}-R_3$$

Pesticide	R_1	R_2	R_3[a]
Aldicarb	$-CH_3$	$-H$	$-ON{=}CH-(CH_3)_2SCCH_3$
Barban		$-H$	$-OCH_2C{=}CCH_2Cl$
Butylate	$-CH_2CH(CH_3)_2$	$-CH_2CH(CH_3)_2$	$-SC_2H_5$
Carbaryl	$-CH_3$	$-H$	
Carbofuran	$-CH_3$	$-H$	
Chloropropham		$-H$	$-OCH(CH_3)_2$
Cycloate		$-C_2H_5$	$-SC_2H_5$
Di-allate	$-CH(CH_3)_2$	$-CH(CH_3)_2$	$-SCH_2CCl{=}CHCl$
EPTC	$-C_3H_7$	$-C_3H_7$	$-SC_2H_5$
Metalkamate	-[b]	-[b]	-[b]
Molinate	(1)—hexamethyl	—(2)[c]	$-SC_2H_5$
Pebulate	$-nC_4H_9$	$-C_2H_5$	$-SC_3H_7$
Propham		$-H$	$-CH(CH_3)_2$
Tri-allate	$-CH(CH_3)_2$	$-CH(CH_3)_2$	$-SCH_2CCl{=}CCl_2$
Vernolate	$-nC_3H_7$	$-nC_3H_7$	$-SC_3H_7$

[a] Pesticides with S in the R_3 group are thiocarbamates.

[b] Mixture of *m*-(Ethylpropyl)phenyl methylcarbamate and *m*-(1-methylbutyl)phenyl methylcarbamate in an approximate ratio of 3:1.

[c] A clearer representation for the structure of molinate is as follows:



Thousands of carbamates have been tested over the years for insecticidal activity. Among the most widely used insecticides of this type, besides carbaryl, are carbofuran, methomyl, aldicarb, propoxur, and metalkamate. Generally, the advantages of these pesticides over the organophosphorus pesticides are their effectiveness against insects resistant to organophosphorus compounds and their frequently greater safety in handling (11).

Like the organophosphorus compounds, the carbamates kill insects by acting as cholinesterase and acetylcholinesterase inhibitors. Like various organophosphorus compounds, some carbamates also act systemically. Among these are Isolan, carbofuran, aldicarb, and methomyl (11).

Chemical reactions for production of pesticides in the carbamate family are indicated in Figure 7 (7). This figure presents five different classes of reactions utilized in the manufacture of carbamate pesticides. Table 12 lists 23 carbamates and the raw materials for the production of each compound (7).

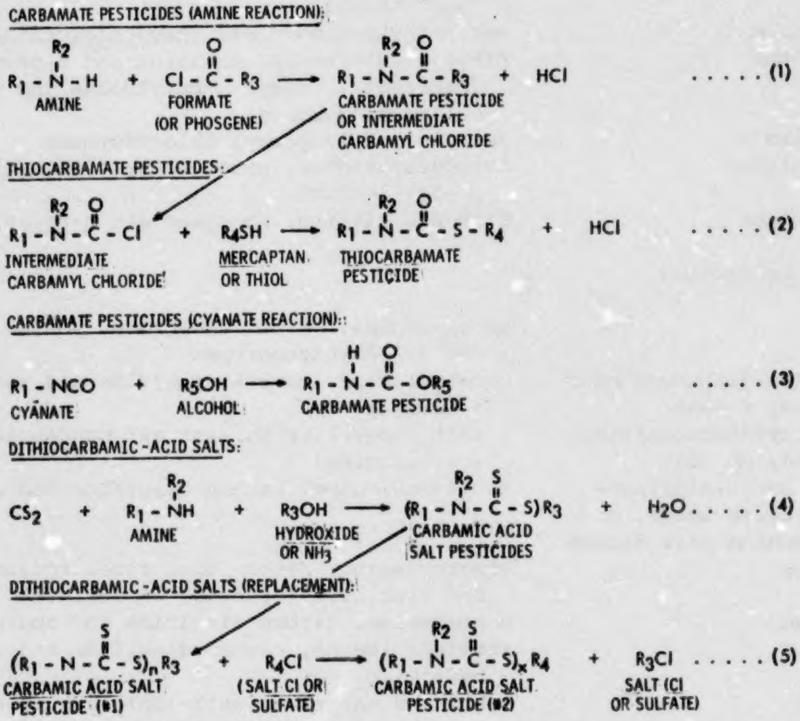

CARBAMATE PESTICIDES (AMINE REACTION):
R1 - N(R2) - H + Cl - C(O) - R3 → R1 - N(R2) - C(O) - R3 + HCl ..... (1)
AMINE
FORMATE (OR PHOSGENE)
CARBAMATE PESTICIDE OR INTERMEDIATE CARBAMYL CHLORIDE
THIOCARBAMATE PESTICIDES:
R1 - N(R2) - C(O) - Cl + R4SH → R1 - N(R2) - C(O) - S - R4 + HCl ..... (2)
INTERMEDIATE CARBAMYL CHLORIDE
MERCAPTAN OR THIOL
THIOCARBAMATE PESTICIDE
CARBAMATE PESTICIDES (CYANATE REACTION):
R1 - NCO + R5OH → R1 - N(H) - C(O) - OR5 ..... (3)
CYANATE
ALCOHOL
CARBAMATE PESTICIDE
DITHIOCARBAMIC-ACID SALTS:
CS2 + R1 - N(R2)H + R3OH → (R1 - N(R2) - C(S) - S)R3 + H2O ..... (4)
AMINE
HYDROXIDE OR NH3
CARBAMIC ACID SALT PESTICIDES
DITHIOCARBAMIC-ACID SALTS (REPLACEMENT):
(R1 - N - C(S) - S)n R3 + R4Cl → (R1 - N(R2) - C(S) - S)x R4 + R3Cl ..... (5)
CARBAMIC ACID SALT PESTICIDE (#1)
(SALT Cl OR SULFATE)
CARBAMIC ACID SALT PESTICIDE (#2)
SALT (Cl OR SULFATE)

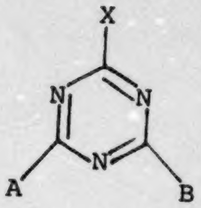
Figure 7. Typical chemical reactions to produce carbamate pesticides (7).

TABLE 12. INPUT MATERIALS FOR CARBAMATE PESTICIDES (7)

Pesticide	Input materials
Carbamates and thio-:	
Aldicarb	Dimethylethylene, sodium nitrate, HCl, methylthiosodium and methylisocyanate
Barban	4-Chloro-2-butynol and 3-chlorophenylisocyanate (Alternate: 4-chloro-2-butynol, 3-chloroaniline)
Butylate	Diiasobutylamine, phosgene and ethyl mercaptan
Carbaryl	1-Napthyl-chloroformate, methylamine and sodium hydroxide
Carbofuran	2,3-Dihydro-2,2-dimethyl-7-benzofuranol and methyl isocyanate
Chloroprophan	*m*-Chloroaniline and isopropyl chloroformate
Cycloate	N-ethylcyclohexylamine and ethylchlorothioformate
Di-allate	Diisopropylamine, phosgene and 2,3-dichloropropenyl-1-thiol
EPTC	Di-*n*-propylamine, phosgene and ethyl mercaptan (Alternate: di-*n*-propylamine and ethylchlorothioformate)
Molinate	Hexamethyleneimine and ethylchlorothioformate
Pebulate	Ethyl-*n*-butylamine, phosgene and n-propyl mercaptan (Alternate: ethyl-*n*-butylamine and n-propylchlorothioformate)
Propham	Aniline and isopropyl chloroformate
Tri-allate	Diisopropylamine, phosgene and 2,3,3-trichlorophenyl-1-thiol
Vernolate	Di-*n*-propylamine, phosgene and n-propyl mercaptan
Dithiocarbamates:	
CDEC	Diethylamine, carbon disulfide, sodium hydroxide and 2,3-dichloropropene
Dimethyldithiocarbamic acid, K salt	Dimethylamine, carbon disulfide and potassium hydroxide
Dimethyldithiocarbamic acid, Mn salt	K salt (above) or Na salt and manganese sulfate (or chloride)
Ethylene-bis(dithiocarbamic acid), diammonium salt ferban	Ethylenediamine, carbon disulfide and ammonia
Ferban	Dimethylamine, carbon disulfide, sodium hydroxide and iron salt (chloride or sulfate)
Metham	Methylamine, carbon disulfide and sodium hydroxide
Nabam	Ethylenediamine, carbon disulfide and sodium hydroxide
Maneb	Nabam and manganese salt (chloride or sulfate)
Zineb	Nabam and zinc salt (chloride or sulfate)

TRIAZINE PESTICIDES

The general structure of triazine pesticides is (7):



where A and B are normally amine groups and X is a less basic group, as shown below.

	A	B	X
Ametryne®	EtNH-[a]	i-PrNH-[b]	$-SCH_3$
Atratone	EtNH-	i-PrNH-	$-OCH_3$
Atrazine	EtNH-	i-PrNH-	-Cl
Bladex®	EtNH-	$(CH_3)_2C(CN)NH-$	-Cl
Chlorazine	Et_2N-	Et_2N-	-Cl
Cyprazine	CH_2CH_2CHN-	$(CH_3)_2CHNH$	-Cl
Dyrene®	ClC_6H_4NH-	Cl-	-Cl
Igran 80W® (terbutryn)	EtNH-	$(CH_3)_3CNH-$	$-SCH_3$
MPMT[c]	$CH_3O(CH_2)_3NH-$	$CH_3O(CH_2)_3NH-$	$-SCH_3$
Prometone	i-PrNH-	i-PrNH-	$-SCH_3$
Prometryne	i-PrNH-	i-PrNH	$-OCH_3$
Propazine	i-PrNH-	i-PrNH-	$-SCH_3$
Simazine	EtNH-	EtNH-	-Cl
Triatazine	EtNH-	EtNH-	-Cl
			-Cl

Derivatives of *s*-triazine form an important class of herbicides. The 1974 estimated U.S. annual production was 68.0 x 10^3 metric tons. Atrazine, the largest selling herbicide in the U.S. today, accounted for 74% of the production of all triazine pesticides (2).

Cyanuric chloride is reacted with appropriate amino hydrocarbons to yield different triazine pesticides as indicated in Figure 8. Table 13 lists raw materials for triazine pesticide manufacture (7).

---

[a] Et is used as an abbreviation for an ethyl subgroup.

[b] i-Pr is used as an abbreviation for an isopropyl subgroup.

[c] 2,4-Bis[(3-methoxy propyl)amino]-6-(methylthio)-*s*-triazine.

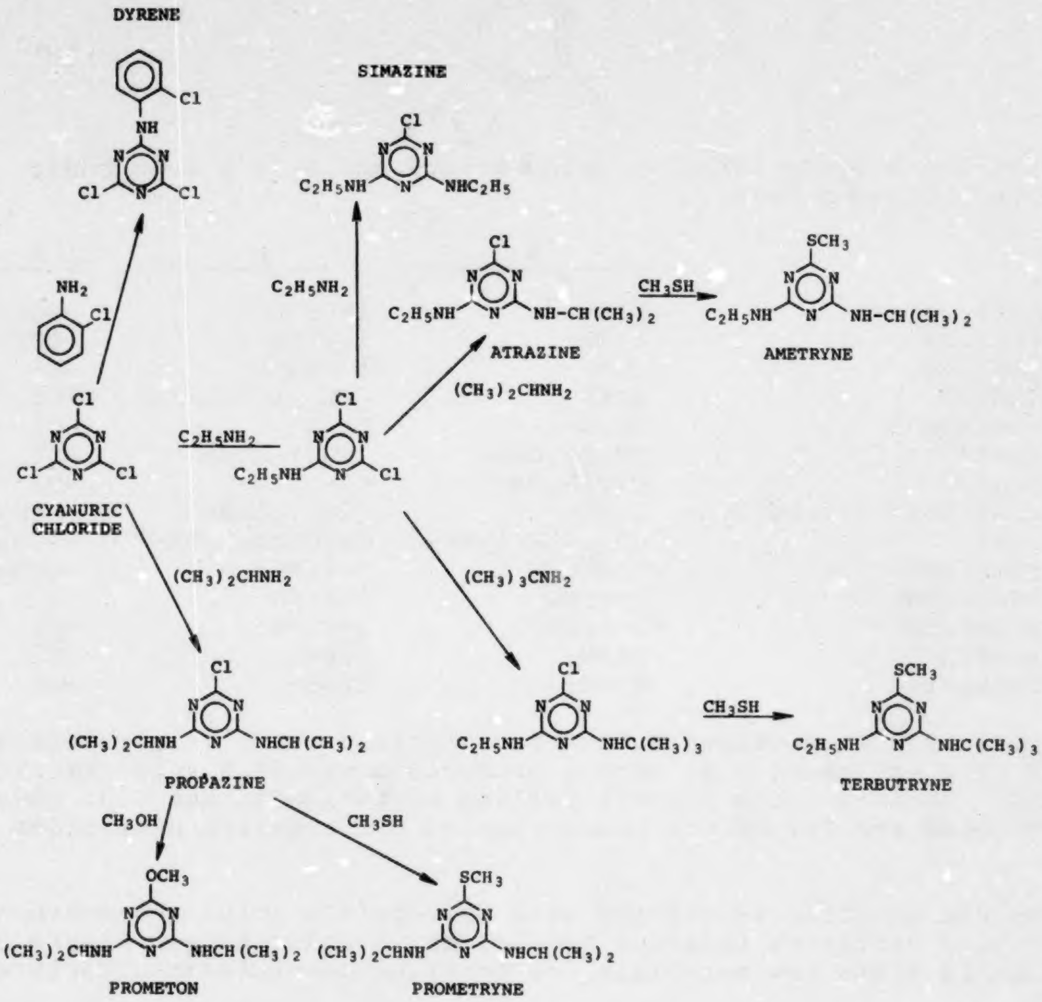

DYRENE
Cl
NH
N
N
Cl
N
Cl
SIMAZINE
Cl
N
N
C2H5NH
N
NHC2H5
NH2
Cl
C2H5NH2
Cl
N
N
C2H5NH
N
NH-CH(CH3)2
CH3SH
SCH3
N
N
C2H5NH
N
NH-CH(CH3)2
ATRAZINE
AMETRYNE
(CH3)2CHNH2
Cl
N
N
Cl
N
Cl
C2H5NH2
Cl
N
N
C2H5NH
N
Cl
CYANURIC
CHLORIDE
(CH3)2CHNH2
(CH3)3CNH2
Cl
N
N
(CH3)2CHNH
N
NHCH(CH3)2
PROPAZINE
Cl
N
N
C2H5NH
N
NHC(CH3)3
CH3SH
SCH3
N
N
C2H5NH
N
NHC(CH3)3
TERBUTRYNE
CH3OH
CH3SH
OCH3
N
N
(CH3)2CHNH
N
NHCH(CH3)2
PROMETON
SCH3
N
N
(CH3)2CHNH
N
NHCH(CH3)2
PROMETRYNE

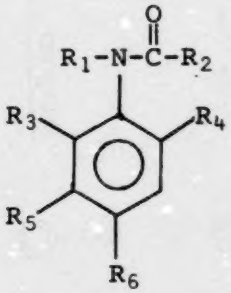
Figure 8. Synthesis of triazine pesticides (7).

TABLE 13. INPUT MATERIALS FOR TRIAZINE PESTICIDES (7)

Pesticide	Input materials (1 mole/mole base)
Ametryne®	Atrazine, methyl mercaptan
Atrazone	Atrazine, methyl alcohol
Atrazine	Cyanuric chloride, ethylamine, $(CH_3)CHNH_2$
Bladex®	Ethylamine, cyanuric chloride $(CH_3)_2C(CN)NH_2$
Chlorazine	Cyanuric chloride, $(C_2H_5)_2NH$, $CIC_6H_4NH_2$
Cyprazine	Cyanuric chloride, CH_2CH_2CHNH
Dyrene®	*o*-Chloroaniline, cyanuric chloride
Igran 80W® (terbutryn)	Cyanuric chloride, ethylamine, $(CH_3)_3CNH_2$, methyl mercaptan
MPMT	Cyanuric chloride, $CH_3O(CH_2)_3NH_2$ (2 moles)
Prometone	Propazire, methyl mercaptan
Prometryne	Propazine, methyl alcohol
Propazine	Cyanuric chloride, $(CH_3)_2CHNH$ (2 moles)
Simazine	Cyanuric chloride, ethylamine (2 moles)

ANILIDE PESTICIDES

Anilide pesticides are a small group of important herbicides which includes propachlor, alachlor, propanil, and butachlor as the major pesticides. These pesticides are derived from aniline and possess the following general structure (7):



Pesticide	R_1	R_2	R_3	R_4	R_5	R_6
Alachlor	CH_3OCH_2	CH_2Cl	C_2H_5	C_2H_5	H	H
Butachlor	$C_4H_9OCH_2$	CH_2Cl	C_2H_5	C_2H_5	H	H
Propachlor	$(CH_3)_2CH$	CH_2Cl	H	H	H	H
Propanil	H	C_2H_5	H	H	Cl	Cl

Total estimated 1974 production for this group was 49.9 x 10^3 metric tons. Propachlor (20.4 x 10^3 metric tons) and alachlor (18.1 x 10^3 metric tons) accounted for over three-fourths of the group's 1974 production (2). Figure 9 presents synthesis reactions for four anilide pesticides, and Table 14 lists input materials for their manufacture (7).

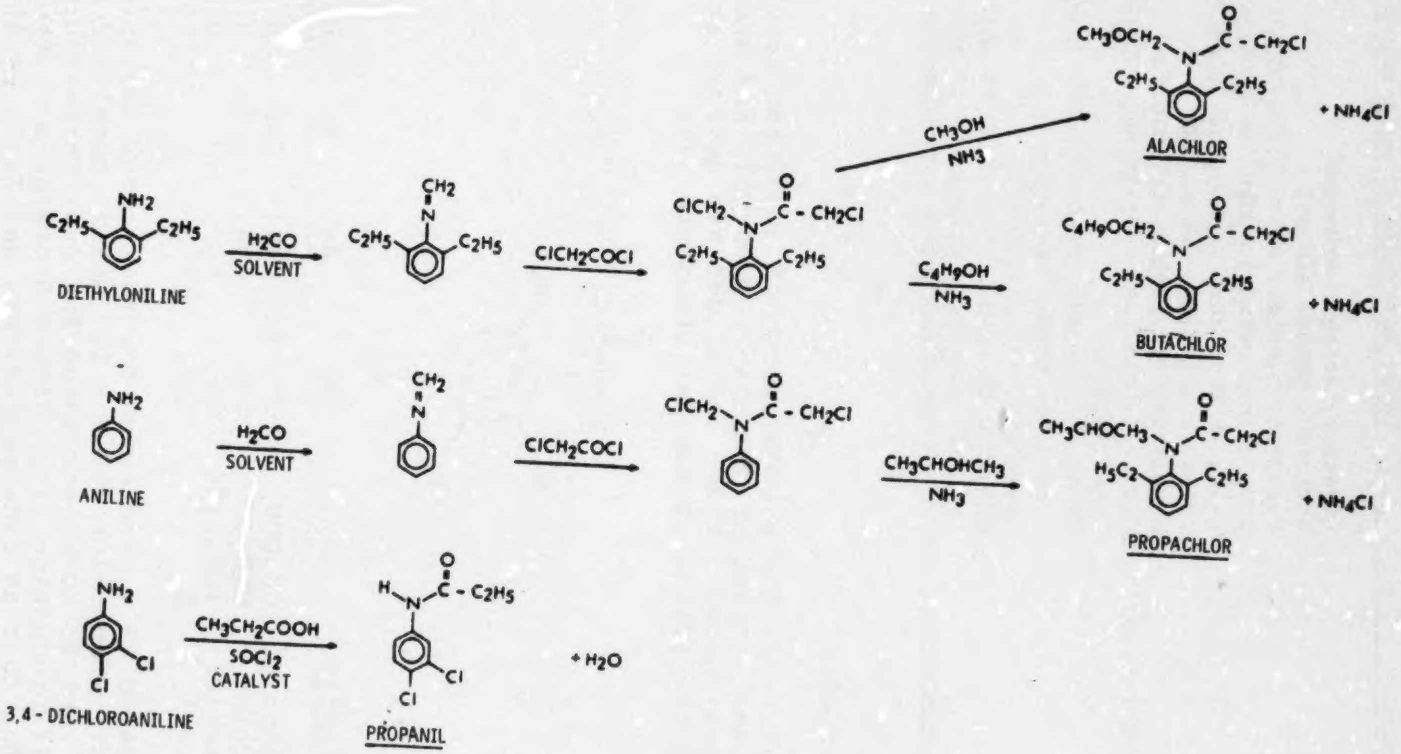

DIETHYLONILINE
H2CO
SOLVENT
ClCH2COCl
CH3OH
NH3
ALACHLOR
+ NH4Cl
C4H9OH
NH3
BUTACHLOR
+ NH4Cl
ANILINE
H2CO
SOLVENT
ClCH2COCl
CH3CHOHCH3
NH3
PROPACHLOR
+ NH4Cl
3,4 - DICHLOROANILINE
CH3CH2COOH
SOCl2
CATALYST
PROPANIL
+ H2O

Figure 9. Chemical reactions for production of anilide pesticides (7).

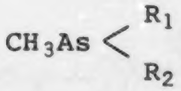
TABLE 14. INPUT MATERIALS FOR FOUR ANILIDE PESTICIDES (7)

Pesticide	Input materials
Alachlor	Diethylaniline, *p*-formaldehyde, chloroacetyl chloride, anhydrous ammonia, methanol
Butachlor	Diethylaniline, *p*-formaldehyde, chloroacetyl chloride, anhydrous ammonia, butanol
Propachlor	Aniline, *p*-formaldehyde, chloroacetyl chloride, anhydrous ammonia, isopropanol
Propanil	3,4-Dichloroaniline, propionic acid, thionyl chloride

ORGANOARSENIC AND ORGANOMETALLIC PESTICIDES

The organoarsenical and organometallic pesticides are a small group of about 15 pesticides. The organoarsenical pesticides are herbicides, and the organometallic pesticides are predominantly mercury and copper fungicides.

The organoarsenic pesticides are all derived from sodium arsenite. DSMA, the derivative, is also the intermediate chemical for producing MSMA, methane arsenic acid and cacodylic acid as indicated in Figure 10 (7). The structure of the organoarsenic pesticides is (7):



$$CH_3As<\begin{matrix}R_1\\R_2\end{matrix}$$

Pesticide	R_1	R_2
DSMA	-ONa	-ONa
MSMA	-ONa	-OH
MAA[a]	-OH	-OH
Cacodylic acid	$-CH_3$	-OH

The two main organomercuric pesticides are formed with benzene from mercuric acetate and mercuric oleate to form PMA and phenyl mercuric oleate. The major organocopper pesticide is formed by reacting naphthenic acids with soluble copper salts to form copper naphthenates.

The 1974 estimated production of organoarsenic and organometallic pesticides totaled 24.9 x 10^3 metric tons. MSMA and DSMA combined for over 81% of this group's 1974 production. Copper naphthenates were the leading organometallic pesticides

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[a] Methanearsonic acid.

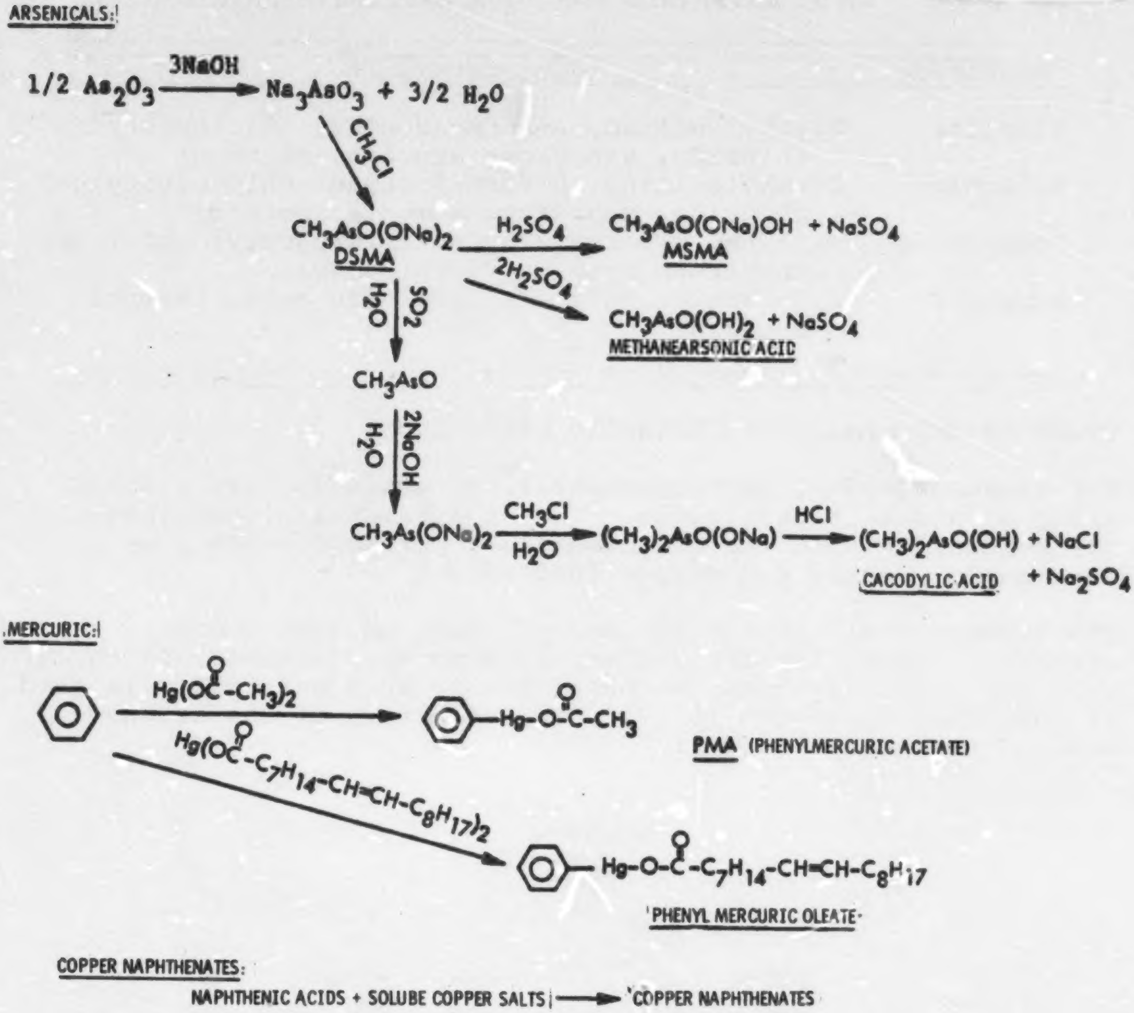

ARSENICALS:
1/2 As2O3
3NaOH
Na3AsO3 + 3/2 H2O
CH3Cl
CH3AsO(ONa)2
DSMA
H2SO4
CH3AsO(ONa)OH + NaSO4
MSMA
2H2SO4
CH3AsO(OH)2 + NaSO4
METHANEARSONIC ACID
H2O
SO2
CH3AsO
H2O
2NaOH
CH3As(ONa)2
CH3Cl
H2O
(CH3)2AsO(ONa)
HCl
(CH3)2AsO(OH) + NaCl
CACODYLIC ACID
+ Na2SO4
MERCURIC:
Hg(OC-CH3)2
Hg-O-C-CH3
PMA (PHENYLMERCURIC ACETATE)
Hg(OC-C7H14-CH=CH-C8H17)2
Hg-O-C-C7H14-CH=CH-C8H17
PHENYL MERCURIC OLEATE
COPPER NAPHTHENATES:
NAPHTHENIC ACIDS + SOLUBE COPPER SALTS
COPPER NAPHTHENATES

Figure 10. Chemical reactions to produce organoarsenic and organometallic pesticides (7).

with 900 metric tons (2). The chemical reactions used to produce these pesticides are indicated in Figure 10, and Table 15 presents their input materials (7).

OTHER NITROGENOUS PESTICIDES

Other nitrogenous pesticides include all nitrogen-containing pesticides which are not included in the carbamate, triazine, anilide, urea, and nitrated hydrocarbon industrial segments. This group includes derivatives of imines, amines, cyanides, hydrazines, and guanidines (7).

TABLE 15. INPUT MATERIALS FOR ARSENICAL AND METALLIC PESTICIDES (7)

Pesticide	Input materials
Organoarsenical:	
DSMA	Arsenic trioxide, sodium hydroxide, methyl chloride
MSMA	DSMA (or materials) and sulfuric acid
Methyl arsenic acid	DSMA (or materials) and sulfuric acid
Cacodylic acid	DSMA (or materials), sulfur dioxide, sodium hydroxide, and hydrochloric acid
Organometallics:	
PMA[a]	Mercuric acetate and benzene
Phenyl mercuric oleate	Mercuric oleate and benzene
Copper naphthenates	Copper salts and naphthenic acids

[a] Phenylmercuric acetate.

The estimated production of other nitrogenous pesticides in 1974 was 31.7 x 10^3 metric tons. The imide fungicides had the largest 1974 production with captan at 9.1 x 10^3 metric tons. Methomyl, an insecticide, was next 4.5 x 10^3 metric tons, followed by CDAA, a preemergence herbicide at 3.2 x 10^3 metric tons (2).

The structures of and chemical reactions used to produce many of these compounds are shown in Figure 11. The imide pesticides (captafol, captan and folpet) have a similar reaction of a sulphenyl chloride with an imide and NaOH. Many other nitrogenous pesticides also have a similar reaction between a chloride and an amine or other nitrogenous compound. No information is available for the reactions that produce methomyl and benomyl, which are both classified as amate pesticides (7).

Raw materials utilized in the manufacture of 15 pesticides in this group are presented in Table 16 (7).

DIENE-BASED CHLORINATED PESTICIDES

Diene-based chlorinated pesticides are derived from hexachlorocyclopentadiene. This group includes the following 13 pesticides: aldrin, dieldrin, heptachlor, chlordane, isodrin, endrin, endosulfan, isobenzan (telodrin), alodan, bromodan, kepone, mirex, and pentac. Toxaphene has a similar chemical structure and is sometimes grouped together with the dienes as the aldrin-toxaphene group (7).

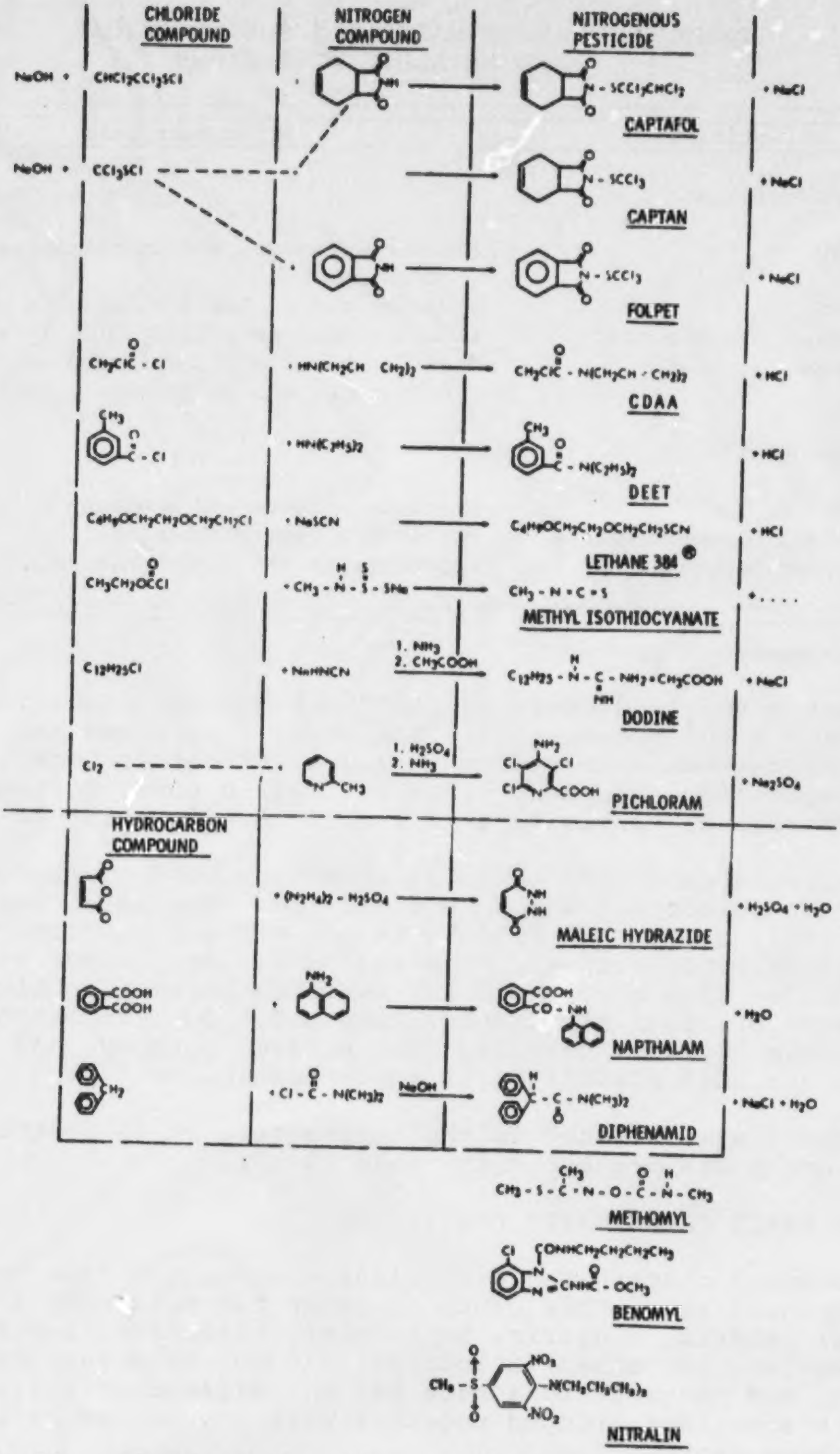
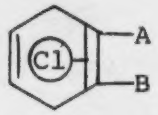

CHLORIDE COMPOUND
NITROGEN COMPOUND
NITROGENOUS PESTICIDE
NaOH + CHCl2CCl2SCl
N - SCCl2CHCl2
CAPTAFOL
+ NaCl
NaOH + CCl3SCl
N - SCCl3
CAPTAN
+ NaCl
N - SCCl3
FOLPET
+ NaCl
CH3CIC - Cl
+ HN(CH2CH CH2)2
CH2CIC - N(CH2CH = CH2)2
CDAA
+ HCl
CH3
C - Cl
+ HN(C2H5)2
CH3
C - N(C2H5)2
DEET
+ HCl
C4H9OCH2CH2OCH2CH2Cl
+ NaSCN
C4H9OCH2CH2OCH2CH2SCN
LETHANE 384 ®
+ HCl
CH3CH2OCCl
+ CH3 - N - S - SNa
CH3 - N = C = S
METHYL ISOTHIOCYANATE
+ . . . .
C12H25Cl
+ NaHNCN
1. NH3
2. CH3COOH
C12H25 - N - C - NH2 • CH3COOH
NH
DODINE
+ NaCl
Cl2
CH3
1. H2SO4
2. NH3
NH2
Cl
Cl
Cl
COOH
PICHLORAM
+ Na2SO4
HYDROCARBON COMPOUND
+ (N2H4)2 - H2SO4
NH
NH
MALEIC HYDRAZIDE
+ H2SO4 + H2O
COOH
COOH
NH2
COOH
CO - NH
NAPTHALAM
+ H2O
CH2
+ Cl - C - N(CH3)2
NaOH
C - C - N(CH3)2
DIPHENAMID
+ NaCl + H2O
CH3
CH3 - S - C = N - O - C - N - CH3
METHOMYL
Cl
CONHCH2CH2CH2CH3
N
N
CHNC - OCH3
BENOMYL
CH3 - S
NO2
-N(CH2CH2CH3)2
NO2
NITRALIN

Figure 11. Chemical reactions and structures for imides, amides and other nitrogenous pesticides (7).

TABLE 16. INPUT MATERIALS FOR OTHER NITROGENOUS PESTICIDES (7)

Pesticide	Input materials
Captafol	Sodium hydroxide, 1,1,2,2-tetrachloroethylsulphenyl chloride and tetrahydrophthalimide
Captan	Sodium hydroxide, trichloromethylsulphenyl chloride and tetrahydrophthalimide
Folpet	Sodium hydroxide, trichloromethylsulphenyl chloride and phthalimide
CDAA	Chloroacetyl chloride and diallyamine
Diphenamid	Sodium hydroxide, dimethylcurbamyl chloride and diphenylmethane
Deet	*m*-Toluyl chloride and diethylamine
Naphthalam	Phthalic acid and 1-naphthylamine
Methomyl	(Data not available)
Benomyl	(Data not available)
Lethane 384	Butyl "carbitol" chloride and sodium thiocyanate
Methyl isothiocyanate	Ethyl chlorocarbamate and N-methyldithiocarbamate
Nitralin	4-Chloro-3-nitrophenyl methylsulfone
Maleic hydrazide	Maleic anhydride and dihydrazine sulfate
Dodine	Dodecyl chloride, sodium cyanide, ammonia and acetic acid
Pichloram	Chlorine, α-picoline, sulfuric acid and ammonia

The structure of many diene pesticides is of the form (7):



where the Cl denotes a saturated chlorinated loop and A and B are side chains. A and B are quite often linked together to form another loop, as indicated for some diene pesticides in Figure 12, which summarizes reaction sequences for diene insecticides.

Estimated 1974 production of diene group pesticides include chlordane (6.8×10^3 metric tons), aldrin (4.5×10^3 metric tons), and endrin (1.4×10^3 metric tons) (2). The production trend is downwards since aldrin and dieldrin have been banned by the U.S. Environmental Protection Agency (EPA) because of high toxicity and low degradable, long-term persistence. Some uses of heptachlor have also been canceled, and chlordane is being reviewed. Mirex, which received widespread use for fire ants, is also restricted by the EPA.

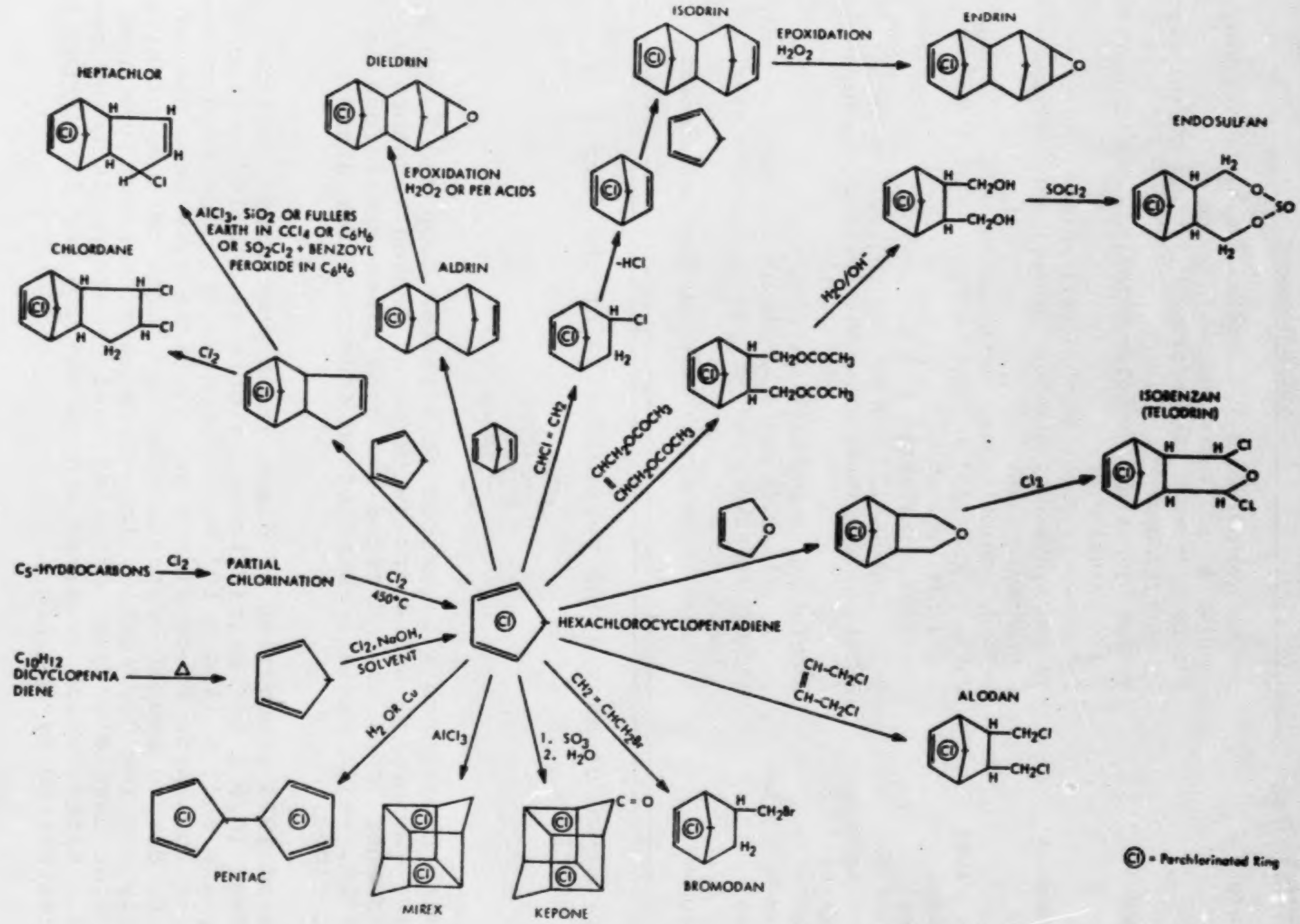

HEPTACHLOR
DIELDRIN
ISODRIN
EPOXIDATION H2O2
ENDRIN
ENDOSULFAN
EPOXIDATION H2O2 OR PER ACIDS
AlCl3, SiO2 OR FULLERS EARTH IN CCl4 OR C6H6 OR SO2Cl2 + BENZOYL PEROXIDE IN C6H6
CHLORDANE
ALDRIN
-HCl
H2O/OH⁻
SOCl2
Cl2
CHCl = CH2
CHCH2OCOCH3 ‖ CHCH2OCOCH3
ISOBENZAN (TELODRIN)
C5-HYDROCARBONS
PARTIAL CHLORINATION
Cl2 450°C
HEXACHLOROCYCLOPENTADIENE
C10H12 DICYCLOPENTA DIENE
Δ
Cl2, NaOH, SOLVENT
H2 OR Cu
AlCl3
1. SO3 2. H2O
CH2 = CHCH2Br
CH-CH2Cl ‖ CH-CH2Cl
ALODAN
PENTAC
MIREX
KEPONE
BROMODAN
Cl = Perchlorinated Ring

Figure 12. Synthesis of the diene group of chlorinated insecticides--from hexachlorocyclopentadiene (12).

Figure 12 indicates the synthesis reaction of the 13 pesticides in the diene group, and Table 17 lists the raw materials used in their production (7, 12).

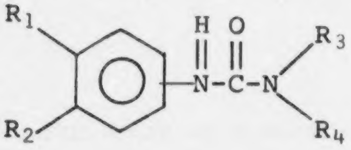
TABLE 17. INPUT MATERIALS FOR DIENE-BASED PESTICIDES (7)

Pesticide	Input materials
Aldrin	Hexachlorocyclopentadiene; bicyclo-(2.2.1)-2,5 heptadiene
Dieldrin	Aldrin; H_2O_2; acetic acid
Chlordane	Hexachlorocyclopentadiene; cyclopentadiene; Cl_2
Heptachlor	Hexachlorocyclopentadiene; cyclopentadiene; $AlCl_3$ or SO_2Cl_2 + benzoyl peroxide in benzene
Isodrin	Hexachlorocyclopentadiene; vinyl chloride (or acetylene); cyclopentadiene
Endrin	Isodrin (or ingredients); H_2O_2; acetic acid
Endosulfan	Hexachlorocyclopentadiene; *cis*-2-butane-1,4-diol; thionyl chloride
Isobenzan (telodrin)	Hexachlorocyclopentadiene (2 moles); 2,5-dihydrofuran; Cl_2
Alodan	Hexachlorocyclopentadiene; $CH-CH_2Cl$ $CH-CH_2Cl$
Bromodan	Hexachlorocyclopentadiene; $CH_2 = CHCH_2Br$
Kepone	Hexachlorocyclopentadiene; SO_3; H_2O
Mirex	Hexachlorocyclopentadiene; $AlCl_3$
Pentac	Hexachlorocyclopentadiene; H_2 or Cu

UREA AND URACIL PESTICIDES

Urea and uracil pesticides are commonly used as herbicides. These pesticides can be synthesized from urea as a common base, but they are more frequently synthesized from an isocyanate compound. Phosgene is used in the synthesis of most urea and uracil pesticides as indicated in the synthesis reactions presented in Figure 13 (7).

Most urea pesticides have the common chemical structure of (7):



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(12) Lawless, E. W., R. von Rümker, and T. L. Ferguson. Pesticide Study Series - 5: The Pollution Potential in Pesticide Manufacturing (PB 213 782). U.S. Environmental Protection Agency, Cincinnati, Ohio, June 1972. 249 pp.

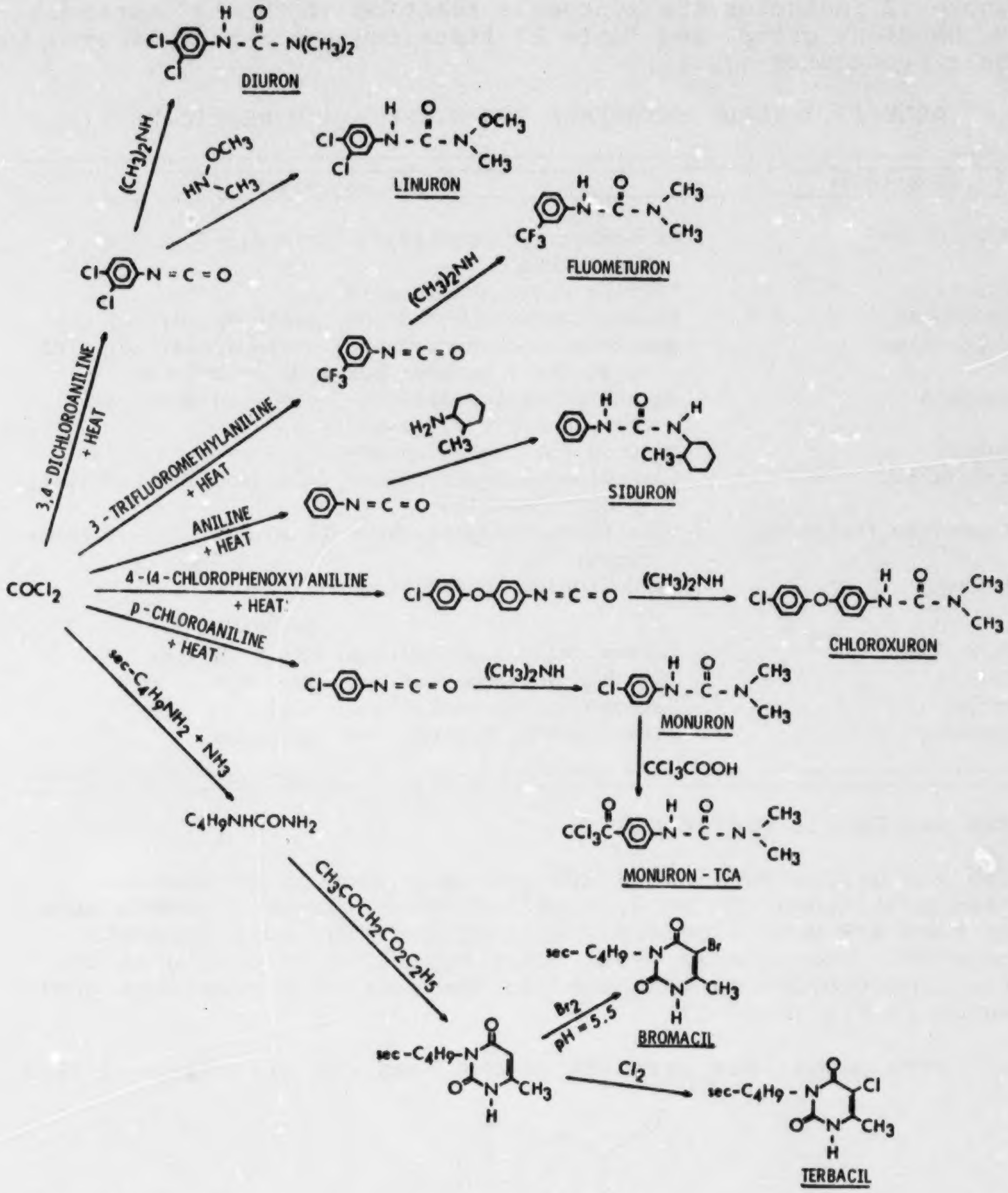
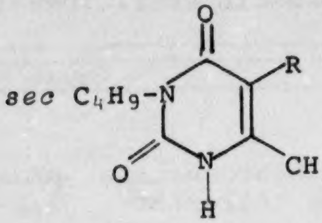

DIURON
$(CH_3)_2NH$
LINURON
FLUOMETURON
$(CH_3)_2NH$
3,4-DICHLOROANILINE + HEAT
3-TRIFLUOROMETHYLANILINE + HEAT
SIDURON
ANILINE + HEAT
$COCl_2$
4-(4-CHLOROPHENOXY) ANILINE + HEAT
$(CH_3)_2NH$
CHLOROXURON
p-CHLOROANILINE + HEAT
$(CH_3)_2NH$
MONURON
CCl_3COOH
MONURON - TCA
$sec\text{-}C_4H_9NH_2 + NH_3$
$C_4H_9NHCONH_2$
$CH_3COCH_2CO_2C_2H_5$
Br_2
pH = 5.5
BROMACIL
Cl_2
TERBACIL

Figure 13. Chemical reactions to form urea and uracil pesticides.

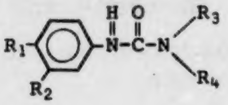
with the R groups indicated in Table 18 for each pesticide. Other urea pesticides (noruron, isonoruron, cycluron and norea) have a similar structure with a replacement for the phenoxy ring.

The uracils have a common structure of the form (7):



where R is "-Br" for bromacil and "-Cl" for terbacil.

TABLE 18. UREA PESTICIDES STRUCTURE (7)



	R_1	R_2	R_3	R_4
Pesticide:				
Chloroxuron	-4-chlorophenoxy	-H	$-CH_3$	$-CH_3$
Diuron	-Cl	-Cl	$-CH_3$	$-CH_3$
Fluometuron	-H	$-CF_3$	$-CH_3$	$-CH_3$
Linuron	-Cl	-Cl	$-OCH_3$	$-CH_3$
Monuron	-Cl	-H	$-CH_3$	$-CH_3$
Monuron-TCA	$-COOCl_3$	-H	$-CH_3$	$-CH_3$
Siduron	-H	-H	-H	-2-methycyclohexane
Other urea pesticides:				
Fenuron	-H	-H	$-CH_3$	$-CH_3$
Neburon	-Cl	-Cl	$-CH_3$	-n-butyl
Buturon	-Cl	-H	$-CH_3$	-1-butyn-3-yl
Monolinuron	-Cl	-H	$-OCH_3$	$-CH_3$
Metabromuron	-Br	-H	$-OCH_3$	$-CH_3$
Chlorobromuron	-Br	-Cl	$-OCH_3$	$-CH_3$
Metoxuron	-OCH	-Cl	$-CH_3$	$-CH_3$

The production of urea and uracil pesticides in 1974 was estimated as 18.1×10^3 metric tons. Bromacil, a uracil pesticide, had an estimated 1974 production of 5.4×10^3 metric tons. The urea pesticide with the largest production in 1974 was diuron at 4.5×10^3 metric tons (2). Table 19 lists input materials used to produce seven urea pesticides and two uracil pesticides (7).

NITRATED HYDROCARBON PESTICIDES

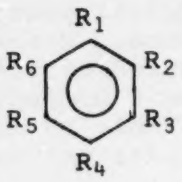
Nitrated hydrocarbon pesticides include several compounds containing one or two of the characteristic nitro($-NO_2$) groups in their chemical structure. Four major pesticides in this group are dinitroaromatics (trifluralin, benefin, dinoseb, and DNOC)

TABLE 19. INPUT MATERIALS FOR UREA AND URACIL PESTICIDES (7)

Pesticide	Input materials
Ureas:	
Diuron	3,4-Dichloroaniline, phosgene and dimethylamine (Alternate: 3,4-dichloroaniline, urea and dimethylamine)
Linuron	3,4-Dichloroaniline, phosgene and O,N-dimethyl hydroxylamine
Fluometuron	3-Trifluoromethyl aniline, phosgene and dimethylamine
Siduron	Aniline, phosgene and 2-methylcyclohexylamine
Chloroxuron	4-(4-Chlorophenoxy) aniline, phosgene and dimethylamine
Monuron	*p*-Chloroaniline, phosgene and dimethylamine (Alternate: *p*-chloroaniline, urea and dimethylamine)
Monuron-TCA	Monuron and trichloroacetic acid
Uracils:	
Bromacil	*sec*-Butylamine, phosgene, ammonia, ethylacetoacetate and bromine
Terbacil	*sec*-Butylamine, phosgene, ammonia, ethylacetoacetate and chlorine

and one is a chlorinated nitrohydrocarbon (chloropicrin) (7). Other pesticides in this group include Basalin®, isopropalin, oryzalin, butralin, dinitramine, Prowl® and Dinocap®.

The general structure of the four nitroaromatic pesticides is (7):



with the individual "R" groups indicated below.[a]

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[a] The formula for chloropicrin is CCl_3NO_2.

Pesticide	R_1	R_2	R_3	R_4	R_5	R_6
Dinoseb	-OH	$-CH(CH_3)CH_2CH_3$	-H	$-NO_2$	-H	$-NO_2$
DNOC[a]	-OH	$-CH_3$	-H	$-NO_2$	-H	$-NO_2$
Trifluralin	$-N(CH_2CH_2CH_2)$	$-NO_2$	-H	$-CF_3$	-H	$-NO_2$
Benefin	$-CH_3CH_2NCH_2CH_2CH_2CH_3$	$-NO_2$	-H	$-CF_3$	-H	$-NO_2$

Estimated 1974 production of the nitrated hydrocarbon pesticides was 18.1×10^3 metric tons. The dinitroaromatic pesticides are herbicides, and chloropicrin is an insecticide. Trifluralin dominated the production in this group with approximately 11.3×10^3 metric tons in 1974 (2).

Table 20 lists raw materials used in the production of nitrated hydrocarbon pesticides (7). The chemical reactions for the production of dinitroaromatic and other nitrated hydrocarbon pesticides are indicated in Figure 14.

TABLE 20. INPUT MATERIALS FOR NITRATED HYDROCARBON PESTICIDES (7)

Pesticide	Input materials
Trifluralin	HNO_3/H_2SO_4, chloro-4-trifluoromethylbenzene and dipropylamine
Benefin	HNO_3/H_2SO_4, chloro-4-trifluoromethylbenzene and butylethylamine
Dinoseb	HNO_3/H_2SO_4, *o-sec*-butylphenol
DNOC[a]	*o*-Cresol, H_2SO_4 and HNO_3/H_2SO_4
Chloropicrin	Nitromethane, chlorine and sodium hydroxide

[a] 4,6-Dinitro-*o*-cresol.

MICROBIAL AND NATURALLY-OCCURRING PESTICIDES (7)

Two types of microorganisms pathogenic to insects have been developed and are in limited commercial use on several crops today, i.e.; preparations of *Bacillus species*, and nuclear polyhedrosis viruses.

Several commercial products based upon *Bacillus thuringiensis* are currently available on the U.S. market. These products are exempted from the requirement of a tolerance and are registered

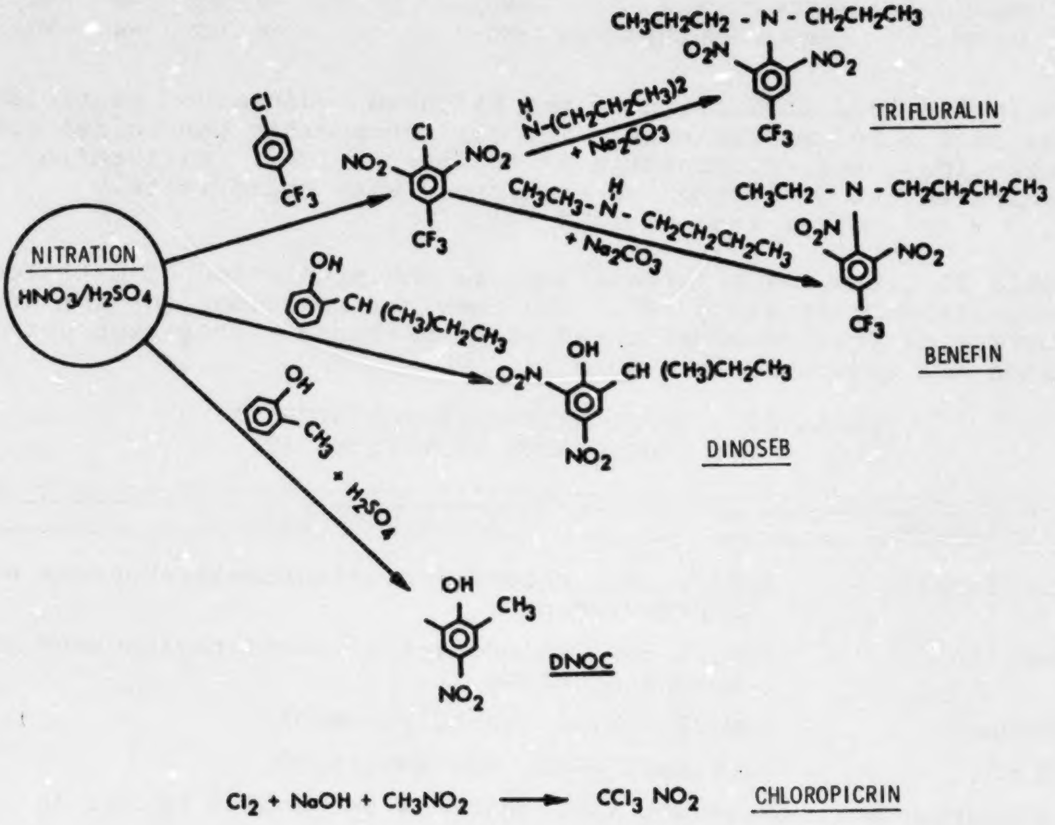
NITRATION
HNO3/H2SO4
TRIFLURALIN
BENEFIN
DINOSEB
DNOC
Cl2 + NaOH + CH3NO2 → CCl3 NO2
CHLOROPICRIN

Figure 14. Chemical reactions to produce the nitrated hydrocarbon pesticides (7).

for the control of lepidopterous insects on a considerable number of crops. The main deterrent to their use is that growers are familiar with the chemical insecticides and their more rapid mode of action, and chemical insecticides are often less expensive per unit control Preparations based on *Bacillus popilliae* and several other *Bacillus* species are under commercial development, but have not yet reached the volume of use of *Bacillus thuringiensis*.

Several nuclear polyhedrosis virus preparations are available in the United States for control of cotton bollworms, but these products are not widely used at this time. Problems concerning their large-scale production, formulation, storage stability, application timing and methods, stability after application, and safety precautions remain to be resolved. Development work is in process on a number of other insect viruses.

Microbial pathogens useful for the nonchemical control of weeds or plant diseases have not been commercially developed to this date.

Natural-occurring pesticides include the pyrethrins, obtusaquinone, and rotenone. The pyrethrins are derived from the chrysanthemum flower, obtusaquinone is an orange pigment of a tropical tree, and rotenone is derived from cube, which is a tropical plant. Pyrethrin pesticides have also been synthesized, and some of these offer promise as insect-specific insecticides.

The processes for production of the microbial and natural-occurring pesticides are at present considerably different from the chemical reactions for other pesticides. The microbial pesticides are developed from cultures in fermented solutions as expressed by the following procedure for *Bacillus thuringiensis*:

$$\text{Nutrient mixture} \xrightarrow{\text{Sterilize}} \xrightarrow{\text{Innoculate}} \xrightarrow{\text{Ferment}} \xrightarrow{\text{Separate}} \xrightarrow{\text{Dry}} \text{Product solid containing} \sim 3\% \text{ B.t.}$$

The pyrethrins are extracted from chrysanthemum flowers as follows:

$$\text{Chrysanthemum flowers } (\textit{Pyrethrum cineraefolium}) \xrightarrow{\text{Solvent}} \text{Crude Extract} \xrightarrow[\text{with } CH_3OH]{\text{Extract}} \xrightarrow[\text{with } C_6H_{14}]{\text{Extract}} \text{Pyrethrin concentrate}$$

The most popular microbial pesticide is *Bacillus thuringiensis* with an estimated production of 450 metric tons in 1972.[a] The total production of microbial and natural-occurring pesticides was about 900 metric tons in 1972. The use of these pesticides is expected to increase significantly in the next decade as new and more effective derivatives are formed and as some of the more toxic and persistent chemical pesticides are forced out by environmental restrictions.

OTHER PESTICIDES

Organic pesticides which are not easily classified in other industry segments include endothall, bensulide, EXD (Herbisan®), Ordam®, acephate, Thanite®, thiabenazole, Terrazole®, diquat, paraquat, and dodine. Other organic pesticides may have been omitted because they are produced only in small quantities. Large-production pesticides, such as elemental sulfur, sodium chlorate, and the organotin compounds were excluded because these materials are products of other industries and are predominantly used for other purposes (7). Creosote has also been excluded since it is a product from coking operations at foundries.

Table 21 lists the raw materials used as input for the production of endothall, bensulide, and EXD. Structures and chemical reactions representing synthesis of these compounds are shown in Figure 15 (7).

TABLE 21. INPUT MATERIALS FOR THREE OTHER ORGANIC PESTICIDES (7)

Pesticide	Input materials
Endothall	Furan and maleic anhydride (plus reducing or oxidizing agent)
Bensulide	N-(β-chloroethyl)benzene sulfonamide and potassium diisopropyl dithiophosphate
EXD[a]	Ethyl alcohol, carbon disulfide, sodium hydroxide and an oxidizer (HCl or H_2SO_4)

[a] Diethyl dithiobis(thionoformate) (Herbisan®).

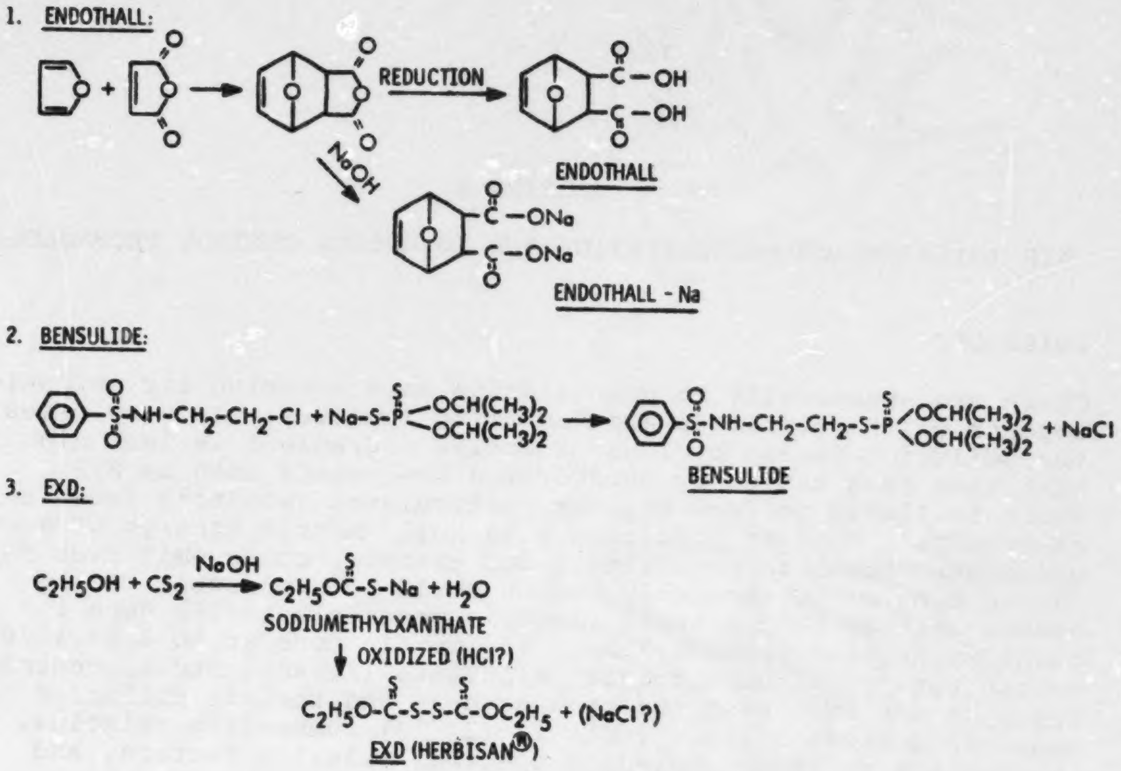
1. ENDOTHALL:
REDUCTION
C—OH
C—OH
ENDOTHALL
NaOH
C—ONa
C—ONa
ENDOTHALL - Na
2. BENSULIDE:
S-NH-CH2-CH2-Cl + Na-S-P —OCH(CH3)2 —OCH(CH3)2
S-NH-CH2-CH2-S-P OCH(CH3)2 OCH(CH3)2 + NaCl
BENSULIDE
3. EXD:
C2H5OH + CS2
NaOH
C2H5OC-S-Na + H2O
SODIUMETHYLXANTHATE
OXIDIZED (HCl?)
C2H5O-C-S-S-C-OC2H5 + (NaCl?)
EXD (HERBISAN®)

Figure 15. Chemical reactions and structures of other pesticides (7).

SECTION 5

AIR EMISSIONS CHARACTERIZATION AND POLLUTION CONTROL TECHNOLOGY

EMISSIONS

There are essentially no quantitative data covering air pollution aspects of the pesticide manufacturing industry. In many cases, the pollution caused by loss of active ingredient is less significant than that caused by unrecovered byproducts such as H_2S, which is flared to form SO_2, or particulates resulting from fuel combustion. A plant producing 4.54×10^3 metric tons/yr of most thioorganophosphate pesticides, for example, could emit over 900 metric tons of SO_2 annually, which would be comparable to the amount emitted from a small electric power plant (2). Such a plant might also produce 2.27×10^3 metric tons/yr to 4.54×10^3 metric tons/yr of particulate pollutants (flyash, etc.), depending upon the fuel used for process heat and the air pollution controls installed (2). Table 22 (2, 13) summarizes principal information regarding emission species, emission factors, and emission rates for seven major pesticides.

Although few quantitative data are available concerning it, evaporation from holding ponds or evaporation lagoons may also be a potential emission source. Liquid wastes from pesticide manufacturing plants often go to a holding pond before treatment or to an evaporation basin for ultimate disposal. Aldrin, for example, was discharged to a $4.05 \times 10^5\text{-m}^2$ asphalt-lined evaporation basin capable of evaporating 0.57 m^3 of water/min (12). Aldrin could have been transferred directly from the lagoon to the atmosphere despite the characteristic low vapor pressure and low solubility. Appendix A presents equations that were used to predict the evaporation rate of several pesticides and develop evaporation emission factors for additional input to the prioritization model. These equations estimate that up to 5.6 kg/day of aldrin could be emitted from the evaporation basin if aldrin was still manufactured.

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(13) Ifeadi, C. N. Screening Study to Development Background Information and Determine the Significance of Air Contaminant Emissions from Pesticide Plants. EPA-540/9-75-026, Washington, D.C., March 1975. 85 pp.

TABLE 22. SUMMARY OF PRINCIPAL AIR EMISSIONS (2, 13)

		Quantity of pollutant emitted	
Pesticide manufactured	Type of pollutant	kg pollutant/ kg active ingredient	kg pollutant/unit time
Methyl parathion	Sulfur dioxide (gas)	0.41	703.7 kg/hr
MSMA	Arsenic trioxide (particulate)	3×10^{-11}	2.92×10^{-8} kg/hr
Trifluralin	Nitrate (particulate)	3.2×10^{-4}[a]	4.54×10^{-1} kg/hr
	Sulfate (particulate)	3.2×10^{-4}[a]	4.54×10^{-1} kg/hr
	Chloride (particulate)	3.2×10^{-4}[a]	4.54×10^{-1} kg/hr
	Sulfur dioxide (gas)	9.5×10^{-4}[a]	1.36 kg/hr
	Sulfur trioxide (gas)	3.2×10^{-4}[a]	4.54×10^{-1} kg/hr
	Hydrogen fluoride (gas)	3.2×10^{-4}[a]	4.54×10^{-1} kg/hr
	Hydrogen chloride (vapor)	3.2×10^{-3}[a]	4.54 kg/hr
	Nitrogen oxide (gas)	9.5×10^{-4}[a]	1.36 kg/hr
Pentachlorophenol	Pentachlorophenol (particulate)	5.5×10^{-4}	-[b]
	Sodium pentachlorophenol (particulate)	2.2×10^{-3}	-[b]
	Phenol (vapor)	1.0×10^{-3}	-[b]
Captan	Captan (particulate)	6.6×10^{-5}[c]	1.82 kg/day
DDT	DDT (particulate)	3.3×10^{-4}[d]	1.14 kg/hr
Toxaphene	Hydrogen chloride (vapor)	(0.53)[e]	(1,974.9 kg/hr)[e]

---

[a] Calculated based on a production rate of 1.13×10^4 metric tons/yr, 330 days/yr, and 24 hr/day.

[b] Blanks indicate data not available.

[c] Calculated based on a production rate of 9.07×10^3 metric tons/yr, 330 days/yr.

[d] Calculated based on a production rate of 2.72×10^4 metric tons/yr, 330 days/yr, and 24 hr/day.

[e] Data given in Reference 13; however, it is believed that this emission is absorbed in a wet scrubber thus reducing emissions by greater than 99%.

EMISSIONS CONTROL

Air emissions from the pesticide industry are generally analogous to emissions from conventional chemical manufacture. Emissions from the manufacturing process, including particulates, gases, and vapors, emanate from various pieces of equipment (for example, reactors, driers, and condensers) and enter the atmosphere as raw materials, intermediates, byproducts, and the active ingredient itself. Several air emission control devices are available, such as baghouses, filters, cyclone separators, electrostatic precipitators, incinerators, and gas scrubbing units for purposes of trapping, separating, washing, and otherwise collecting gases and particulates (2).

The most popular and practically applicable technique used in controlling emissions from the manufacture of pesticides[a] involves wet scrubbing with water. A smaller percentage of plants employ alkali absorption and adsorption processes and baghouses. Wet scrubbing, absorption, and adsorption processes are used mainly for controlling gases and vapors, controlling particulates to a lesser extent. Baghouses are used primarily for controlling particulate emissions. A summary of air emission control devices, emission species controlled, and control efficiency is presented in Table 23 for five major pesticides (13).

SELECTED PESTICIDES

In order to present a general overview concerning atmospheric emissions and air pollution control technology found in the pesticide manufacturing industry, 12 pesticides, corresponding to major products in each of the 12 industry segments, are discussed in the following sections. Information presented, when available, includes emission species, sources and rates; process description; and emissions control technology for the following pesticides:

toxaphene - chlorinated hydrocarbon
methyl parathion - organophosphate
carbaryl - carbamate
atrazine - triazine
alachlor - anilide
MSMA - organoarsenic
captan - other nitrogenous
chlordane - diene-based
bromacil - uracil
trifluralin - nitrated hydrocarbon
Bacillus thuringiensis - microbial
methyl bromide - other

---

[a] Based on a study of methyl parathion, toxaphene, MSMA, trifluralin, pentachlorophenol, and *p*-dichlorobenzene.

TABLE 23. SUMMARY OF AIR EMISSION CONTROL DEVICES FOR FIVE MAJOR PESTICIDES (13)

Pesticide	Control device	Emissions controlled	Reported efficiency, %
Methyl parathion[a]	Incinerator	Hydrogen sulfide, sulfur, mercaptan	–[b]
	Water scrubber	Phosphorus pentoxide, hydrogen chloride	95
	Brink® mist eliminator	Phosphorus pentoxide (for visibility)	99.9
Toxaphene[c]	Alkali and water scrubber	Solvent vapor, hydrogen chloride, chlorine	
	Stripping	Solvent vapor, hydrogen chloride, chlorine	
	Limestone adsorption	Solvent vapor, hydrogen chloride, chlorine	100
	Baghouse	Toxaphene	
MSMA[d,e]	Baghouse	Arsenic trioxide	
	Water scrubber	Arsenic trioxide	
	Acidifier vent scrubbers		
Trifluralin[f]	1- and 2-Stage venturi scrubber and Tri-mer wet scrubber		90
Pentachlorophenol[g]	Packed and venturi scrubber	Chlorine, phenol, acids	90 to 100
	Baghouse	Pentachlorophenol	95 to 99
	Mechanical seals	(For pentachlorophenol reactor)	

[a] Information reported by Monsanto.

[b] Blanks indicate data not available.

[c] Information reported by Hercules.

[d] Information reported by Diamond Shamrock.

[e] Information reported by Ansul.

[f] Information reported by Eli Lilly.

[g] Information reported by Reichhold.

Toxaphene

Toxaphene is an important chlorinated hydrocarbon insecticide containing 67% to 69% chlorine. Toxaphene production involves two main steps: the production of camphene in a reactor from α-pinene, and the reaction of chlorine gas with camphene in a solvent solution at the chlorinator. The raw materials involved in the manufacture of toxaphene are α-pinene, chlorine, solvent, and compounds used in effluent treatment operations (13).

The production and waste handling schematic used by one manufacturer is presented in Figure 16 (13). The gaseous emissions from the chlorinator (chlorine gas, hydrochloric acid, and solvent vapors) are passed through condensers, caustic scrubbers, and a neutralization tower containing limestone, while the solution containing toxaphene is filtered, stripped, and formulated into marketable forms.

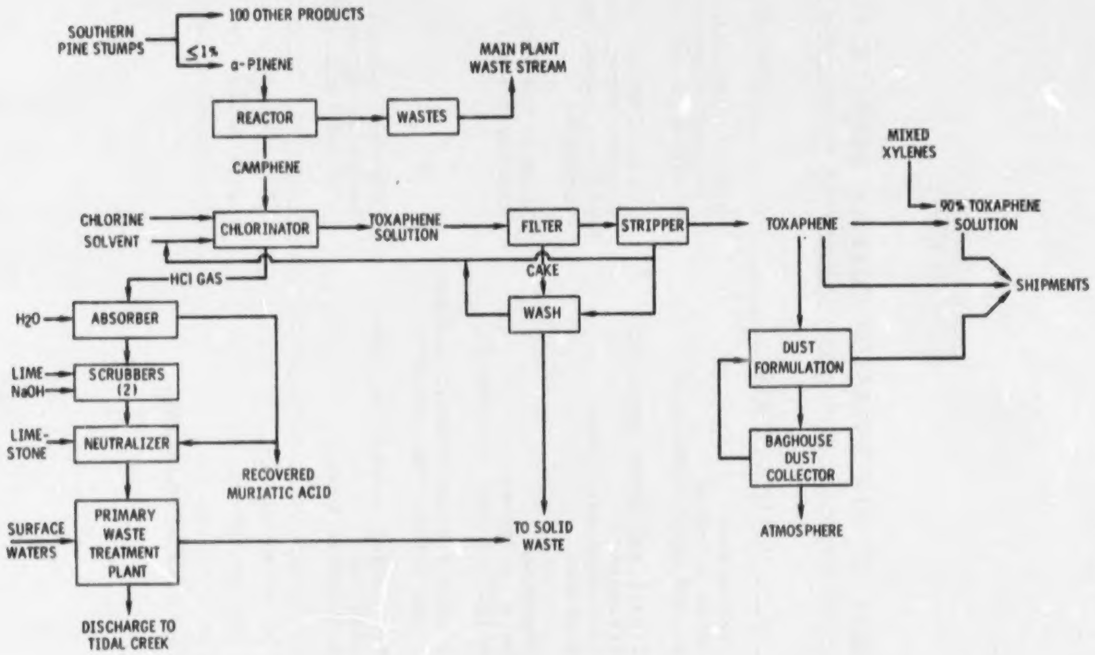

SOUTHERN PINE STUMPS
100 OTHER PRODUCTS
≤1%
α-PINENE
MAIN PLANT WASTE STREAM
REACTOR
WASTES
CAMPHENE
MIXED XYLENES
CHLORINE
SOLVENT
CHLORINATOR
TOXAPHENE SOLUTION
FILTER
STRIPPER
TOXAPHENE
90% TOXAPHENE SOLUTION
CAKE
HCl GAS
SHIPMENTS
H_2O
ABSORBER
WASH
LIME
NaOH
SCRUBBERS (2)
DUST FORMULATION
LIME-STONE
NEUTRALIZER
BAGHOUSE DUST COLLECTOR
RECOVERED MURIATIC ACID
SURFACE WATERS
PRIMARY WASTE TREATMENT PLANT
TO SOLID WASTE
ATMOSPHERE
DISCHARGE TO TIDAL CREEK

Figure 16. Production and waste handling schematic for toxaphene (13).

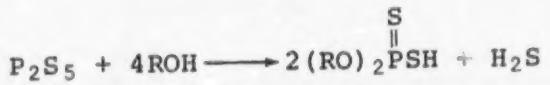
Emission sources from the manufacture of toxaphene include the reactor and the chlorinator. No information is available regarding emissions from α-pinene production. The main emission from the reactor is chlorine gas; emissions from the chlorinator contain quantities of chlorine gas, hydrochloric acid, and solvent vapor. Uncontrolled hydrogen chloride emissions have been estimated to be 0.53 kg/kg active ingredient (13). However, these emissions are known to be controlled by absorption using a wet scrubber (14). Assuming a control efficiency of 99.5%, the estimated hydrogen chloride emission factor from this source would be 2.65 kg/metric ton active ingredient.

There are three main control techniques used for controlling acidic gases produced from toxaphene manufacture: 1) scrubbing (alkali or water), 2) stripping, and 3) adsorption. One plant uses these techniques to control hydrogen chloride, chlorine gas, and solvent vapor emissions (13). The emissions are initially passed through condensers that remove the majority of the solvent and the hydrochloric acid. Caustic scrubbers then remove additional traces of hydrochloric acid and chlorine. The effluent is finally passed through large towers containing limestone. The final rate of emissions is not known.

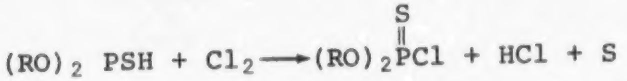
Various control technologies are available in the chemical industry for controlling particulates, such as baghouses, scrubbers, electrostatic precipitators, etc. Baghouses are used at one plant to control toxaphene particle emissions (13). No information is available on this plant's uncontrolled or controlled emissions, nor is control information available from other toxaphene manufacturing plants.

Methyl Parathion

Methyl parathion is a nonpersistent broad spectrum organophosphate insecticide that is highly toxic to humans. It is commonly manufactured from sodium *p*-nitrophenolate by reaction with *O*,*O*-dimethyl phosphorothiochloridate and has the following production chemistry (12):



$$P_2S_5 + 4ROH \longrightarrow 2(RO)_2\overset{\overset{S}{\|}}{P}SH + H_2S \qquad (6)$$



$$(RO)_2PSH + Cl_2 \longrightarrow (RO)_2\overset{\overset{S}{\|}}{P}Cl + HCl + S \qquad (7)$$

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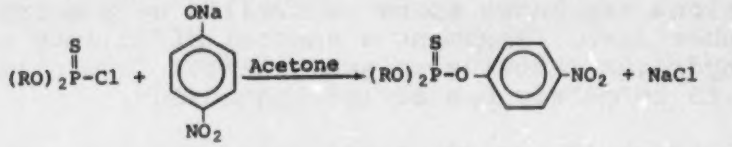
(14) Meiners, A. F., C. E. Mumma, T. L. Ferguson, and G. L. Kelso. Wastewater Treatment Technology Documentation for Toxaphene Manufacture. EPA-440/9-76-013, U.S. Environmental Protection Agency, Washington, D.C., February 1976. 123 pp.


ONa
S
(RO)$_2$P-Cl +
Acetone
S
(RO)$_2$P-O
NO$_2$ + NaCl
NO$_2$

(8)

The raw materials are sodium *p*-nitrophenolate, methyl alcohol, chlorine, and phosphorus pentasulfide. In the production of methyl parathion, byproducts such as sodium chloride (NaCl) and hydrogen chloride (HCl) are formed along with waste products such as H_2S, mercaptan, and sulfur (S) (13). The production and waste schematic for methyl parathion is shown in Figure 17 (13). The odorous compounds (H_2S and mercaptan) from the reactor are flared, and the sulfur-containing species emitted from the chlorinator are incinerated.

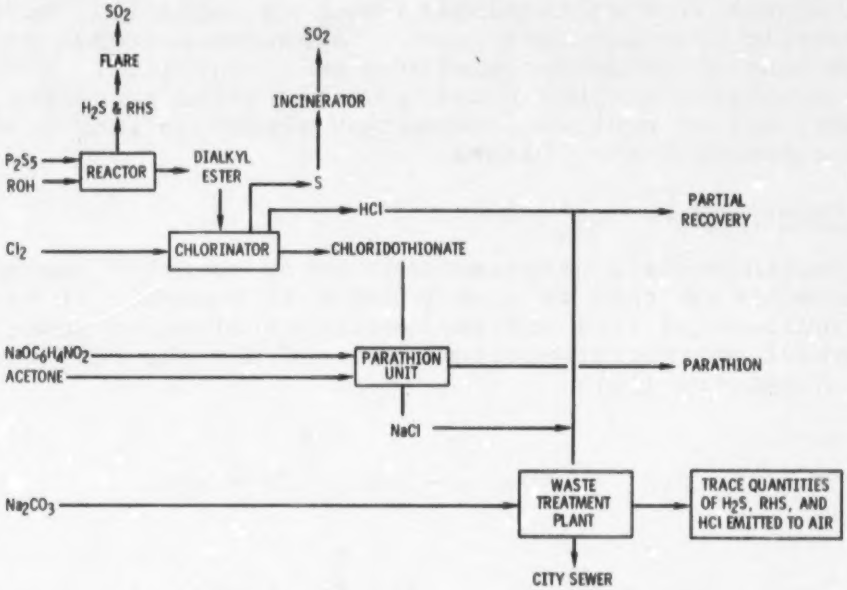

SO$_2$
FLARE
H$_2$S & RHS
SO$_2$
INCINERATOR
P$_2$S$_5$
ROH
REACTOR
DIALKYL ESTER
S
HCl
PARTIAL RECOVERY
Cl$_2$
CHLORINATOR
CHLORIDOTHIONATE
NaOC$_6$H$_4$NO$_2$
ACETONE
PARATHION UNIT
PARATHION
NaCl
Na$_2$CO$_3$
WASTE TREATMENT PLANT
TRACE QUANTITIES OF H$_2$S, RHS, AND HCl EMITTED TO AIR
CITY SEWER

Figure 17. Production and waste handling schematic for methyl parathion (13).

Air contaminant emission sources include the reactor, the chlorinator, and the parathion unit. Odorous pollutants arise from vents, liquid wastes, and residues. During the disposal of byproducts (for example, flaring of H_2S and mercaptans, and incineration of sulfur), sulfur dioxide is given off. Also, during wastewater treatment or lagooning, odorous compounds, such as H_2S, mercaptans, etc., are emitted. Emission rates for H_2S and S prior to incineration of off-gases have been calculated as 208.8 kg/hr, 190.7 kg/hr, and 208.8 kg/hr, respectively, on the basis of 330 days/yr and 24-hr/day operation (13).

Sulfur dioxide emission rates based on H_2S and S oxidation from incineration and flaring are estimated to be 703.7 kg/hr from the following reactions (13):

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O \tag{9}$$

$$S + O_2 \rightarrow SO_2 \tag{10}$$

Air emission sources, emission species, and emission rates are presented in Table 24 (13):

TABLE 24. AIR CONTAMINANT EMISSIONS, SOURCES, AND RATES FROM METHYL PARATHION MANUFACTURE AND WASTE TREATMENT (13)

Sources of emission	Particulates	Rates, kg/hr	Gases/vapors	Rates, kg/hr	Odor
Manufacturing processes:					
Reactor	None	-[a]	Diphosphorus pentoxide Mercaptan Hydrogen sulfide	-	Mercaptan Xylene Hydrogen sulfide
Chlorination	Acid mist, Sulfur	208.8 190.7	Phosphorus trichloride Thiophosphoryl chloride Methanol Methyl chloride Hydrochloric acid	-	-
Parathion unit	Basic mist, Methyl monochloride	208.8	-	-	-
Waste treatment processes:					
Incinerator and flaring	Phosphorus pentoxide	-	Sulfur dioxide Phosphorus pentoxide	703.7	None
Waste treatment plant	None	-	Hydrogen sulfide Mercaptan	-	Hydrogen sulfide Mercaptan
Lagooning	None	-	Hydrogen sulfide Mercaptan	-	Hydrogen sulfide Mercaptan

[a] Not available.

Practical sulfur dioxide emission control processes for H_2S, mercaptan, etc., available for methyl parathion plants are incineration in series with a scrubbing system and carbon adsorption. Control of visible fumes created by the emission of diphosphorus pentoxide can be achieved by a mist eliminator, while H_2S and mercaptan emission control during the wastewater treatment can be achieved by chemical oxidation and deodorization.

The air emission control system used by one plant is shown in Figure 18. Incineration is used to control the off gases and residue, while heavy chlorination is used to control the wastewater odorous emissions. The scrubbing system used to control the incineration emission is quoted to achieve an efficiency of 95% for the removal of diphosphorus pentoxide. The BRINK® mist eliminator provides about 99.9% visibility reduction. Incineration of sulfur may be considered a better practical control method than recovery because the sulfur that can be recovered in this process is inescapably contaminated with toxic methyl parathion (13).

On the basis of available information, this is the only plant manufacturing methyl parathion that is controlling air emissions: the sulfur compounds by incineration, diphosphorus pentoxide by scrubbing, and visibility by a Brink mist eliminator. However, SO_2 produced during the incineration of sulfur compounds is not controlled. An estimated 5.58 x 10^3 metric tons of SO_2 were emitted in 1974 (13).

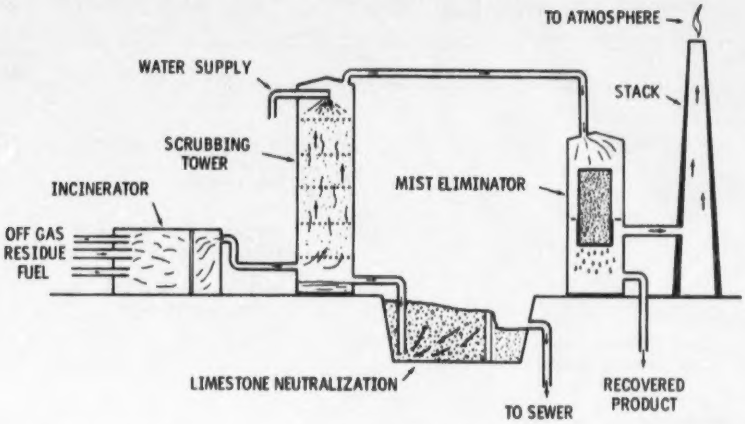
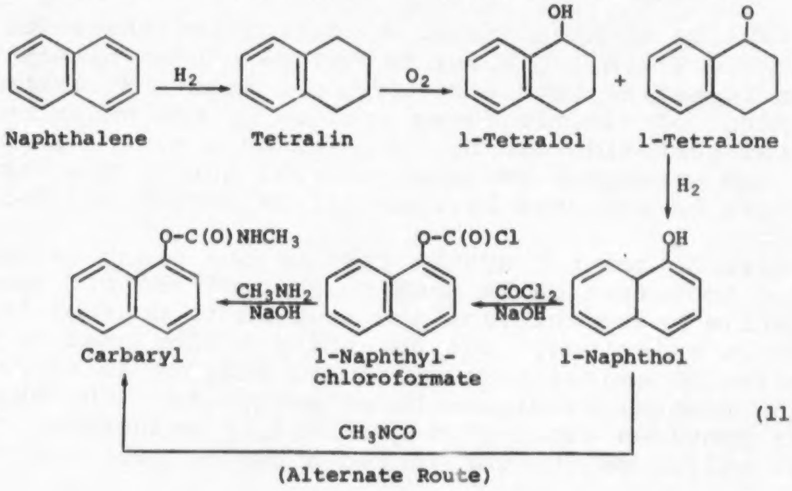

TO ATMOSPHERE
WATER SUPPLY
STACK
SCRUBBING TOWER
INCINERATOR
MIST ELIMINATOR
OFF GAS
RESIDUE
FUEL
LIMESTONE NEUTRALIZATION
TO SEWER
RECOVERED PRODUCT

Figure 18. Parathion residue and off-gas incinerator (13).

Carbaryl

Carbaryl is a moderately toxic, nonpersistent insecticide classified in the "Carbamates" industry segment. One company manufactures carbaryl by a combination of batch and continuous processes with the following production chemistry (12):


H_2
O_2
OH
O
+
Naphthalene
Tetralin
1-Tetralol
1-Tetralone
H_2
O-C(O)NHCH$_3$
O-C(O)Cl
OH
CH_3NH_2
NaOH
$COCl_2$
NaOH
Carbaryl
1-Naphthyl-chloroformate
1-Naphthol
CH_3NCO
(Alternate Route)

(11)

A production and waste schematic for carbaryl is shown in Figure 19 (12).

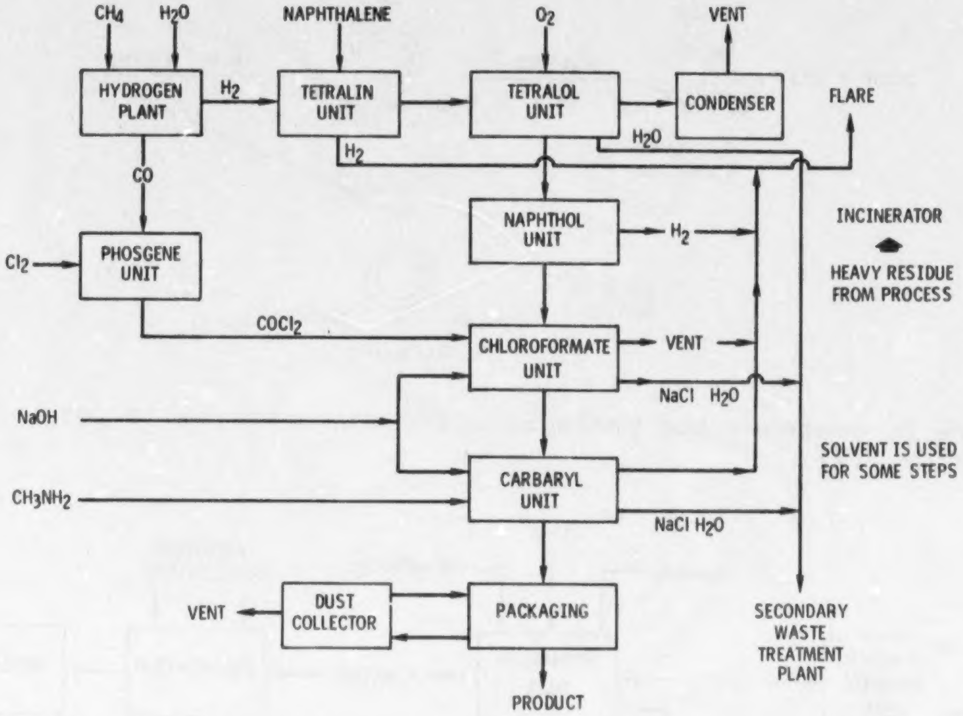

CH4
H2O
NAPHTHALENE
O2
VENT
HYDROGEN PLANT
H2
TETRALIN UNIT
TETRALOL UNIT
CONDENSER
FLARE
H2O
H2
CO
NAPHTHOL UNIT
H2
INCINERATOR
HEAVY RESIDUE FROM PROCESS
Cl2
PHOSGENE UNIT
COCl2
CHLOROFORMATE UNIT
VENT
NaCl H2O
NaOH
SOLVENT IS USED FOR SOME STEPS
CH3NH2
CARBARYL UNIT
NaCl H2O
VENT
DUST COLLECTOR
PACKAGING
SECONDARY WASTE TREATMENT PLANT
PRODUCT

Figure 19. Production and waste schematic for carbaryl (12).

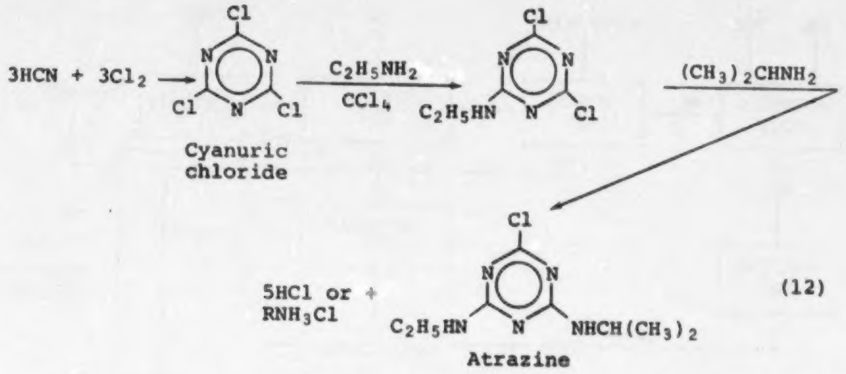
Raw materials utilized in the production of carbaryl include naphthalene, hydrogen, chlorine, oxygen, phosgene, methanol, and sodium hydroxide (50%). Byproduct wastes are liquid streams, vents, and some heavy residues. All toxic vents are flared or vented to the atmosphere, and standard hood systems with recycle of recovered material are used in the packaging process (12). Information concerning sources, rates, and types of emissions is not available.

Atrazine

Atrazine, estimated to be the largest selling herbicide in the United States in 1974, is a selective herbicide classified in the "Triazines" industry segment. Ciba-Geigy Corp., the largest producer of atrazine, has an estimated annual plant capacity of 9×10^4 metric tons (15). The estimated production of atrazine in 1974 was 5 x 10^4 metric tons (2). Atrazine is produced by a continuous process; its reaction chemistry is shown below (12):

---

(15) von Rümker, R., E. W. Lawless, and A. F. Meiners. Production, Distribution, Use and Environmental Impact Potential of Selected Pesticides (PB 238 795). Council on Environmental Quality, Washington, D.C., March 1974. 439 pp.


3HCN + 3Cl2
Cl
N
Cl
Cyanuric chloride
C2H5NH2
CCl4
C2H5HN
(CH3)2CHNH2
5HCl or + RNH3Cl
NHCH(CH3)2
Atrazine

(12)

Figure 20 presents the production and waste schematic for atrazine (12).

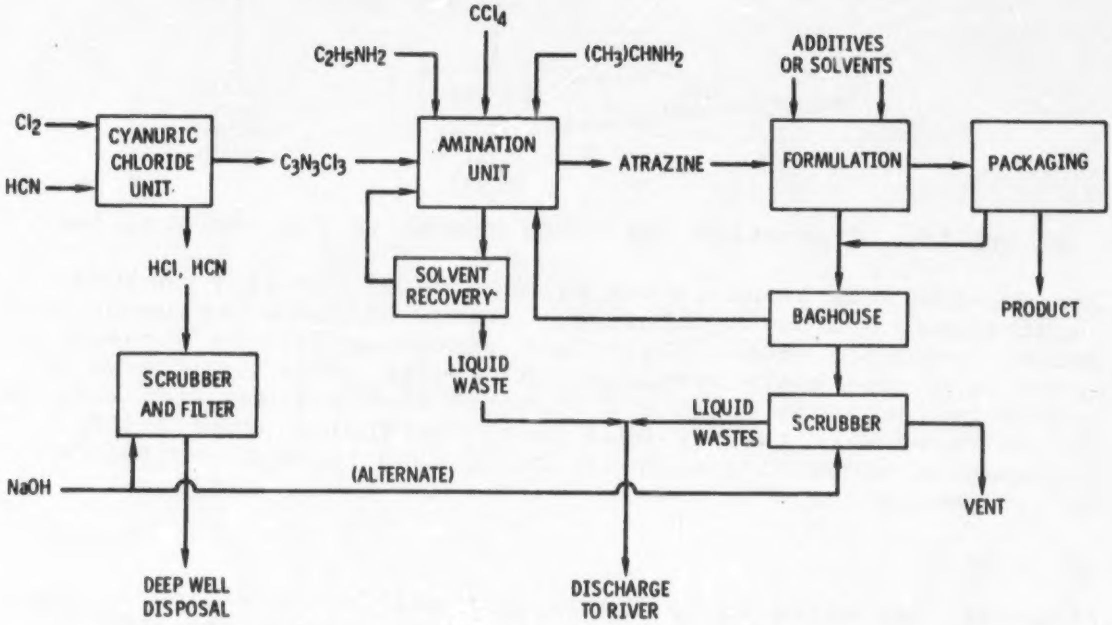

CCl4
C2H5NH2
(CH3)CHNH2
ADDITIVES OR SOLVENTS
Cl2
HCN
CYANURIC CHLORIDE UNIT
C3N3Cl3
AMINATION UNIT
ATRAZINE
FORMULATION
PACKAGING
HCl, HCN
SOLVENT RECOVERY
BAGHOUSE
PRODUCT
SCRUBBER AND FILTER
LIQUID WASTE
LIQUID WASTES
SCRUBBER
NaOH
(ALTERNATE)
VENT
DEEP WELL DISPOSAL
DISCHARGE TO RIVER

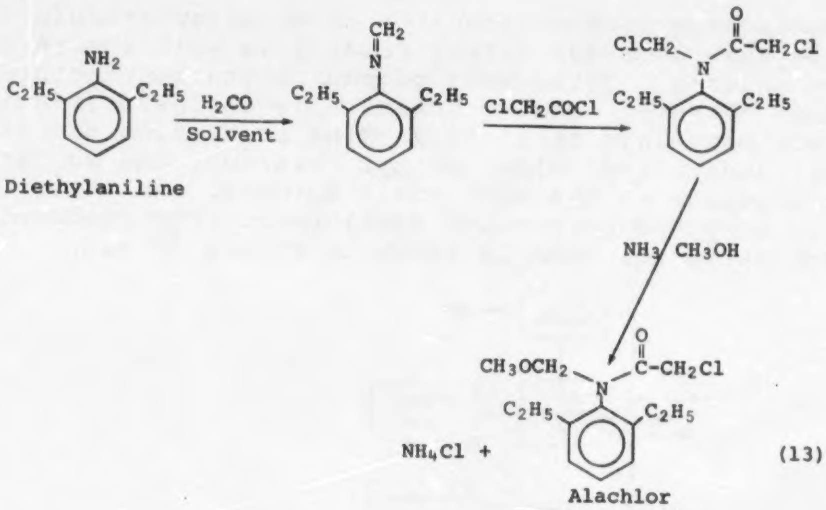
Figure 20. Production and waste schematic for atrazine (12).

Hydrogen chloride and hydrogen cyanide emissions from the cyanuric chloride unit are controlled by a scrubber and filter, as shown in Figure 20 (12). Cyanuric chloride is sublimable and may possibly be entrained from the cyanuric chloride unit and the amination unit. Possible cocondensation of hydrogen cyanide (HCN) could result in emissions of lower HCN condensation products. Possible solvent emissions include carbon tetrachloride. Other potential emissions during the manufacture of atrazine include ethylamine and isopropylamine.

Available information regarding air pollution control is shown diagramatically in Figure 20. Hydrogen chloride from the cyanuric chloride unit is controlled by a scrubber, then discharged to a deep well or river.

Alachlor

Alachlor, a selective herbicide classified in the "Anilides" industry segment, is produced in a batch process with the following production chemistry (12):


NH2
C2H5
C2H5
Diethylaniline
H2CO
Solvent
CH2
N
C2H5
C2H5
ClCH2COCl
O
ClCH2
C-CH2Cl
N
C2H5
C2H5
NH3/ CH3OH
O
CH3OCH2
C-CH2Cl
N
C2H5
C2H5
NH4Cl +
Alachlor

(13)

Raw materials for the production of alachlor include 2,6-diethyl aniline, chloroacetyl chloride ($ClCH_2COCl$), *p*-formaldehyde, methanol, ammonia, and aromatic solvents as shown in the production and waste schematic (Figure 21) (12).

The alachlor process is said to have no solid product and to give off no gases. Production equipment requires cleanup only two to three times per year. No information is available regarding types and sources of emissions, but raw material and solvent losses could occur during handling. Solvents are burned as fuel, but their emission rates are unknown (12).

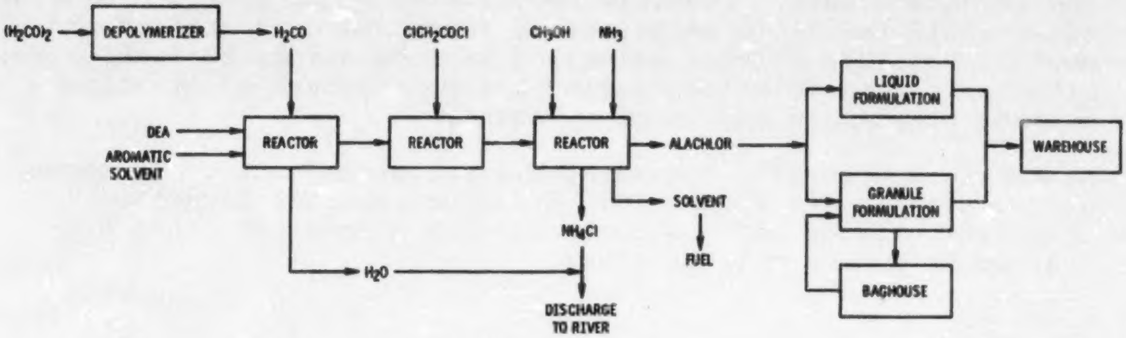

$(H_2CO)_2$
DEPOLYMERIZER
H_2CO
$ClCH_2COCl$
CH_3OH
NH_3
DEA
AROMATIC SOLVENT
REACTOR
REACTOR
REACTOR
ALACHLOR
SOLVENT
FUEL
NH_4Cl
H_2O
DISCHARGE TO RIVER
LIQUID FORMULATION
GRANULE FORMULATION
BAGHOUSE
WAREHOUSE

Figure 21. Production and waste schematic for alachlor (12).

MSMA

MSMA (monosodium methanearsonate) is an organoarsenic selective herbicide that degrades fairly readily in soil and is not highly toxic to animals. Three main compounds are manufactured in the production of MSMA: sodium arsenite, methylarsonic acid, and MSMA. Raw materials utilized in MSMA production are arsenic trioxide, sodium hydroxide, methyl chloride, and sulfuric acid. Arsenic trioxide is the most toxic species, and it is imperative that this compound be handled cautiously. The production and waste schematic for MSMA is shown in Figure 22 (13).

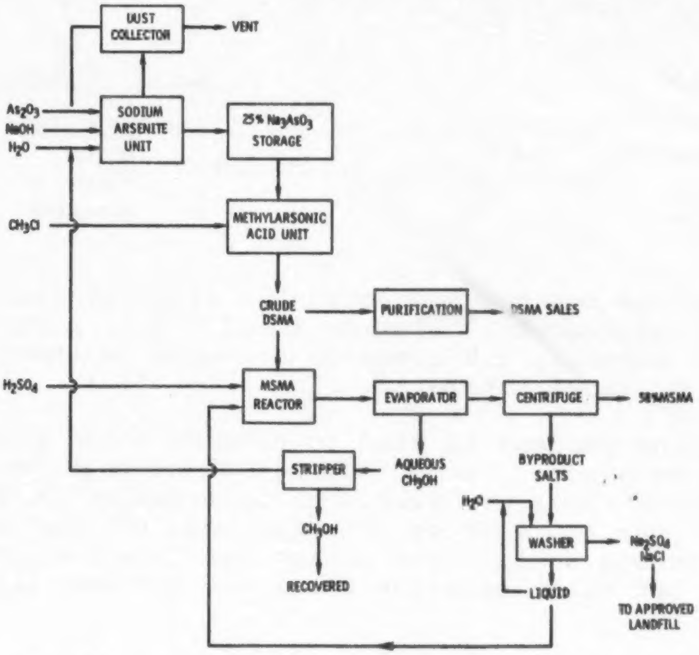

UUST COLLECTOR
VENT
As_2O_3
NaOH
H_2O
SODIUM ARSENITE UNIT
25% Na_3AsO_3 STORAGE
CH_3Cl
METHYLARSONIC ACID UNIT
CRUDE DSMA
PURIFICATION
DSMA SALES
H_2SO_4
MSMA REACTOR
EVAPORATOR
CENTRIFUGE
58%MSMA
STRIPPER
AQUEOUS CH_3OH
BYPRODUCT SALTS
H_2O
WASHER
Na_2SO_4 NaCl
CH_3OH
RECOVERED
LIQUID
TO APPROVED LANDFILL

Figure 22. Production and waste handling schematic for MSMA (13).

The main source of air contaminant emissions during the manufacture of MSMA is in the sodium arsenite production during the unloading of arsenic trioxide. Minor emissions may occur during the processing of the MSMA by evaporation from vents of the reactors.

The main emission during the production of sodium arsenite is arsenic trioxide, which is very toxic. One plant estimates the controlled emission of arsenic trioxide (As_2O_3) to be 3×10^{-9} kg/metric ton or 2.93×10^{-8} kg/hr. During the production of DSMA and MSMA, vapors of methyl chloride (CH_3Cl), sodium sulfate (Na_2SO_4), and methanol are given off (13).

The only air pollutant controlled in this industry is As_2O_3. The compound is emitted as particulates, for which various control techniques are available, such as baghouses, scrubbers, and electrostatic precipitators.

One plant operates the As_2O_3 drum opening and dump bin under a hood equipped with a blower that will pull the As_2O_3 into a bag filter for collection. Another plant controls the arsenic trioxide emission by a scrubbing system. Efficiencies of these control systems are not known by the firms. The best control technique for this highly toxic arsenic trioxide is to have both baghouses and scrubbers in series. The bag filter is useful in recovering As_2O_3, while the scrubber removes the smaller size particles that normally will not be collected by the bag filter (13).

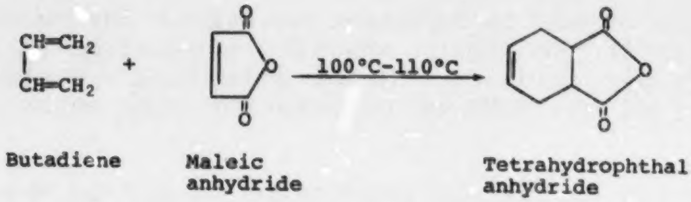
Captan

Captan, classified in the "Other Nitrogenous Compounds" industry segment, is a contact fungicide effective against a fairly broad spectrum of plant pathogenic fungi. It is estimated that 9×10^3 metric tons of captan were produced in the United States in 1974 (2). Captan is manufactured in a two-step reaction process using two intermediates, followed by several purification steps.

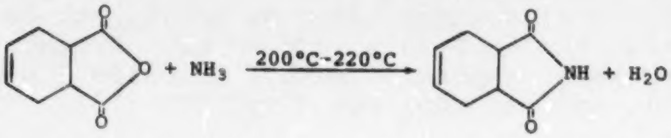
One of these intermediates is tetrahydrophthalimide, which is also made by a two-step reaction (16):

---

(16) Substitute Chemical Program: Initial Scientific and Mini-economic Review of Captan. EPA-540/1-75-012, U.S. Environmental Protection Agency, Washington, D.C., April 1975. 173 pp.



(14)



(15)

Reaction 14 proceeds with a minimum of byproduct. The anhydride is typically above 99% purity and contains minute quantities of vinyl cyclohexene and other butadiene polymeric materials as the major impurities. The reaction is carried out by bubbling butadiene gas into molten maleic anhydride at a temperature of 100°C to 110°C (16).

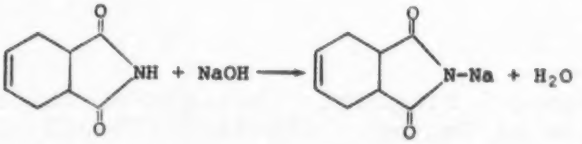
In Reaction 15, a small amount of colored maleimide resin polymers is formed from the reaction of ammonia and unreacted maleic anhydride. The reaction is run at a high temperature to boil off the water, and, during this process, all of the vinyl cyclohexene and most of the other volatile impurities are removed. The purity of the imide is typically 98%, with residual water and tetrahydrophthalic anhydride being the major impurities (16).

The second intermediate is perchloromethyl mercaptan, made by the following reaction (16):

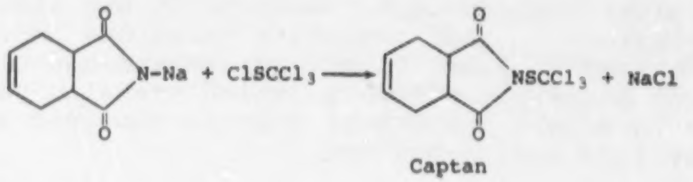
$$CS_2 + 3Cl_2 \xrightarrow{I_2} CCl_3SCl + SCl_2 \qquad (16)$$

Perchloromethyl mercaptan is produced at 0°C to 15°C by Reaction 16, which is exothermic. The pressure is approximately atmospheric or slightly higher. Iodine is a common catalyst, but ferric chloride or aluminum chloride may be used. The final purity is greater than or equal to 96% (16).

The tetrahydrophthalimide is mixed with sodium hydroxide, then reacted with perchloromethyl mercaptan as shown in Reactions 17 and 18 (16):



(17)


N-Na + ClSCCl₃
NSCCl₃ + NaCl
Captan

(18)

Reaction 17 is a mixing-dissolving step, but Reaction 18 (captan production) is controlled at a temperature between 10°C and 30°C, and at essentially atmospheric pressure. The reaction, taking from 10 to 40 minutes, is carried out in an aqueous medium of pH 10.0 to 10.5, using no catalyst. The pH must be kept as low as possible to prevent decomposition of the product, but high enough to drive the reaction to completion by absorbing the HCl formed (16).

The production and waste schematic for captan is shown in Figure 23 (12). Raw materials include carbon disulfide, iodine, chlorine, ammonia, calcium carbonate, maleic anhydride, butadiene, and sodium hydroxide. Possible solvents used include ketones and aromatic, aliphatic or chlorinated hydrocarbons.

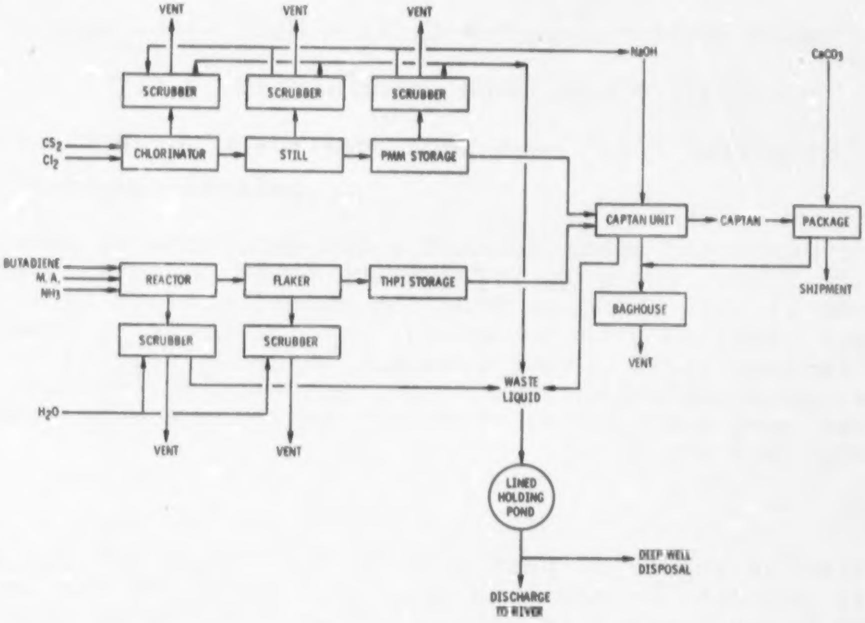

VENT
VENT
VENT
NaOH
CaCO₃
SCRUBBER
SCRUBBER
SCRUBBER
CS₂
Cl₂
CHLORINATOR
STILL
PMM STORAGE
CAPTAN UNIT
CAPTAN
PACKAGE
BUTADIENE
M.A.
NH₃
REACTOR
FLAKER
THPI STORAGE
SHIPMENT
BAGHOUSE
VENT
SCRUBBER
SCRUBBER
WASTE LIQUID
H₂O
VENT
VENT
LINED HOLDING POND
DEEP WELL DISPOSAL
DISCHARGE TO RIVER

Figure 23. Production and waste schematic for captan (12).

The only data available on air emissions indicate that captan is lost in the form of particulates at a rate of about 1.8 kg/day (2). Possible additional emission species include hydrogen chloride, ammonia, carbon disulfide, iodine, chlorine, and butadiene, due to their volatility. The perchloromethyl mercaptan and sulfur dichloride produced by Reaction 16 are also present as possible emissions. Other potential emissions include maleic anhydride, which may sublime; vinyl cyclohexene and other low molecular weight butadiene polymers, which are also volatile; and impurities in maleic anhydride, such as succinic anhydride, which may volatilize during boiling.

Air pollution controls include: 3.78-m^3/s baghouse stacks for controlling captan particulates, a 3.07-m^3/s filter hood exhaust to contain steam and particulates, and a 1.65-m^3/s packer baghouse stack to control particulates (12).

Chlordane

Chlordane is a persistent broad spectrum insecticide classified in the "Diene-Based" industry segment. Chlordane is manufactured by a continuous process, and the process reactions are approximately as follows (15):

$$\text{Naphtha} \longrightarrow \text{Cyclopentadiene } (C_5H_6) \qquad (19)$$

$$Cl_2 + \text{NaOH (aq.)} \longrightarrow \text{NaClO (aq.)} \qquad (20)$$

$$\text{NaClO (aq.)} + C_5H_6 \longrightarrow C_5Cl_6 + \text{NaCl (alk. soln.)} \qquad (21)$$

$$C_5Cl_6 + C_5H_6 \longrightarrow \text{Chlordene } (C_{10}H_6Cl_6) \qquad (22)$$

$$\text{Chlordene} + Cl_2 \longrightarrow \text{Tech. chlordane } (C_{10}H_6Cl_8 + \text{related epoxides}) \qquad (23)$$

The production and waste schematic for chlordane is shown in Figure 24 (15). The only information found concerning air emissions is that chlorine from the chlorine tanks is forced out under pressure with no losses, meeting Chlorine Institute Specifications (12). Other possible emission species include naphtha, cyclopentadiene, and lower halogenated "chlordanes", which are very sublimable. However, emission sources and emission rates are not known.

Bromacil

Classified as the major pesticide in the "Ureas and Uracils" industry segment, bromacil is used as a herbicide for general weed and brush control in noncrop areas. The production steps are similar for all members of this industry segment, although starting materials differ. The chemical synthesis for bromacil is (17):

---

(17) Substitute Chemical Program: Initial Scientific and Minieconomic Review of Bromacil. EPA-540/1-75-006, U.S. Environmental Protection Agency, Washington, D.C., March 1975. 79 pp.

sec-butylamine + phosgene + ammonia → *sec*-butylurea + 2HCl (24)

sec-butylurea + ethyl acetoacetate → 3-*sec*-butyl-6-methyluracil + H_2O + ethanol (25)

3-*sec*-butyl-6-methyluracil + $Br_2 \xrightarrow{\text{pH 5.5}}$ bromacil + HBr (26)

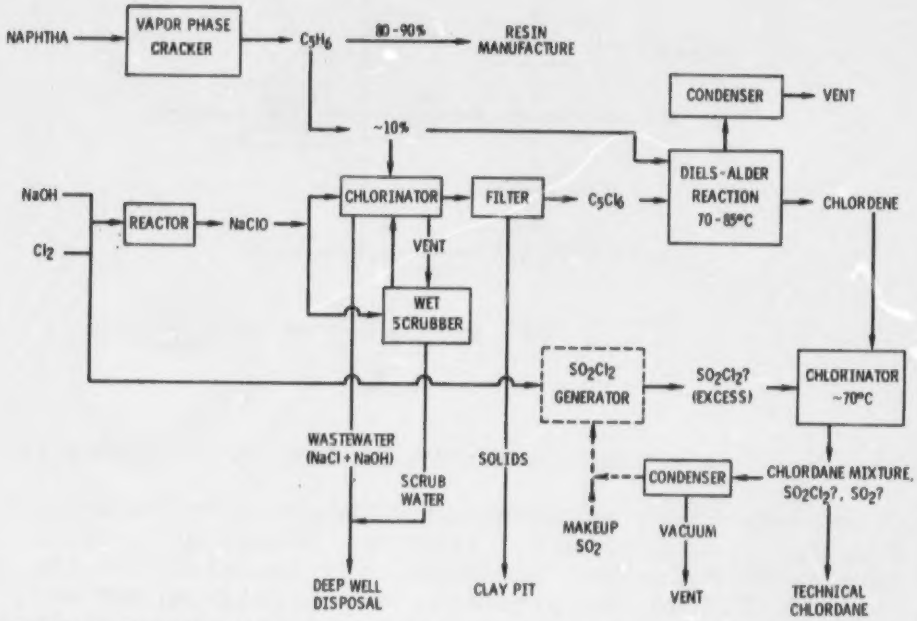

NAPHTHA
VAPOR PHASE CRACKER
C_5H_6
80-90%
RESIN MANUFACTURE
~10%
CONDENSER
VENT
NaOH
Cl_2
REACTOR
NaClO
CHLORINATOR
FILTER
C_5Cl_6
DIELS-ALDER REACTION 70-85°C
CHLORDENE
VENT
WET SCRUBBER
SO_2Cl_2 GENERATOR
SO_2Cl_2? (EXCESS)
CHLORINATOR ~70°C
WASTEWATER (NaCl + NaOH)
SCRUB WATER
SOLIDS
CONDENSER
CHLORDANE MIXTURE, SO_2Cl_2?, SO_2?
MAKEUP SO_2
VACUUM
DEEP WELL DISPOSAL
CLAY PIT
VENT
TECHNICAL CHLORDANE

Figure 24. Production and waste schematic for chlordane (15).

The E. I. du Pont de Nemours Company is the sole manufacturer of bromacil. The manufacturing plant, located in La Porte, Texas, has an estimated total capacity of 9 x 10^3 metric tons per year for all substituted uracils (17). Actual 1974 bromacil production was estimated as approximately 6 x 10^3 metric tons (2).

The preparation of bromacil is described as follows (17):

> "A solution of 182 parts of 3-*sec*-butyl-6-methyluracil in 700 parts of acetic acid containing 82 parts of sodium acetate was treated with 160 parts of bromine. After standing overnight, the mixture, which contained some solid, was evaporated to a solid under reduced pressure. The solid was recrystallized from an ethanol-water mixture to give, as a white crystalline solid, 2-*sec*-butyl-5-bromo-6-methyluracil melting at 157.5°C to 160°C".

A proposed schematic for bromacil is presented in Figure 25 (15).

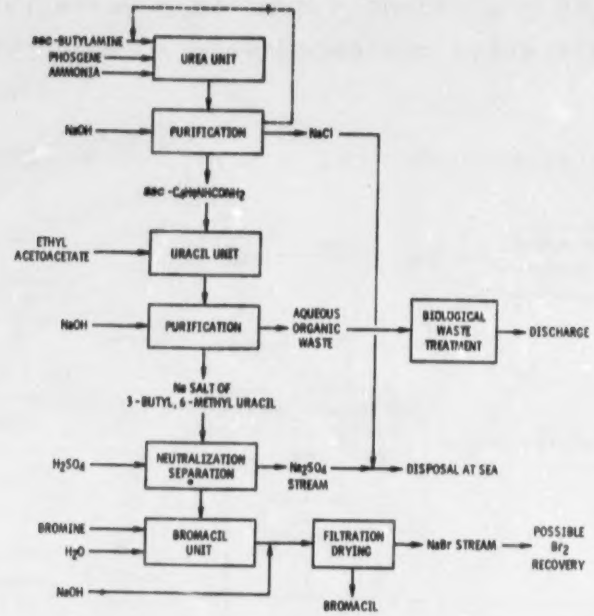

sec-BUTYLAMINE
PHOSGENE
AMMONIA
UREA UNIT
NaOH
PURIFICATION
NaCl
sec-C4H9NHCONH2
ETHYL ACETOACETATE
URACIL UNIT
NaOH
PURIFICATION
AQUEOUS ORGANIC WASTE
BIOLOGICAL WASTE TREATMENT
DISCHARGE
Na SALT OF 3-BUTYL, 6-METHYL URACIL
H2SO4
NEUTRALIZATION SEPARATION
Na2SO4 STREAM
DISPOSAL AT SEA
BROMINE
H2O
NaOH
BROMACIL UNIT
FILTRATION DRYING
NaBr STREAM
POSSIBLE Br2 RECOVERY
BROMACIL

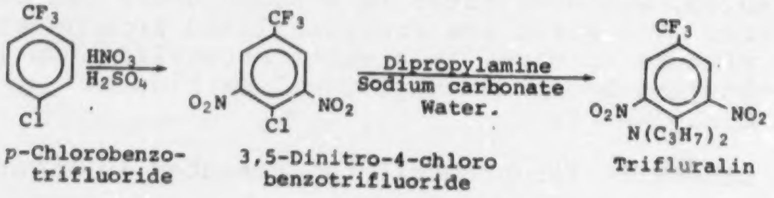
Figure 25. Production and waste schematic for bromacil (15).

No data are available on emission rates or species generated during bromacil manufacture. Possible emissions include the raw materials *sec*-butylamine, phosgene, and ammonia from the urea unit, in addition to the products, *sec*-butylurea and HCl. Ethyl acetoacetate and ethanol are possibly emitted from the uracil unit and bromine from the bromacil unit. Acetic acid, used as a solvent in the bromacil unit, may also be emitted to the atmosphere. A cross reaction product in the manufacture of bromacil may be acetone, which may also be an emission species.

No information was found concerning air pollution control in the manufacture of bromacil.

Trifluralin

Trifluralin is a selective preemergence herbicide classified in the "Nitrated Hydrocarbon" industry segment. The manufacture of trifluralin involves two main steps: nitration and amination. The simple process chemistry is given as follows (13):


CF3
HNO3
H2SO4
Cl
p-Chlorobenzotrifluoride
CF3
O2N
NO2
Cl
3,5-Dinitro-4-chloro benzotrifluoride
Dipropylamine
Sodium carbonate
Water.
CF3
O2N
NO2
N(C3H7)2
Trifluralin

(27)

Nitration involves the reaction of the following compounds in reactors: *p*-chlorobenzotrifluoride, sulfuric acid, and nitric acid. The product of the reaction is 3,5-dinitro-4-chlorobenzotrifluoride, and the byproduct is spent sulfuric acid which is recycled. The main off gases are nitrogen oxides (13).

Amination, the second-stage reaction, involves the reaction of 3,5-dinitro-4-chlorobenzotrifluoride, dipropylamine, and sodium carbonate in solution. The product of the reaction is trifluralin and the effluent is brine solution which is treated for recovery (13).

The production and waste schematic for trifluralin is presented in Figure 26 (13).

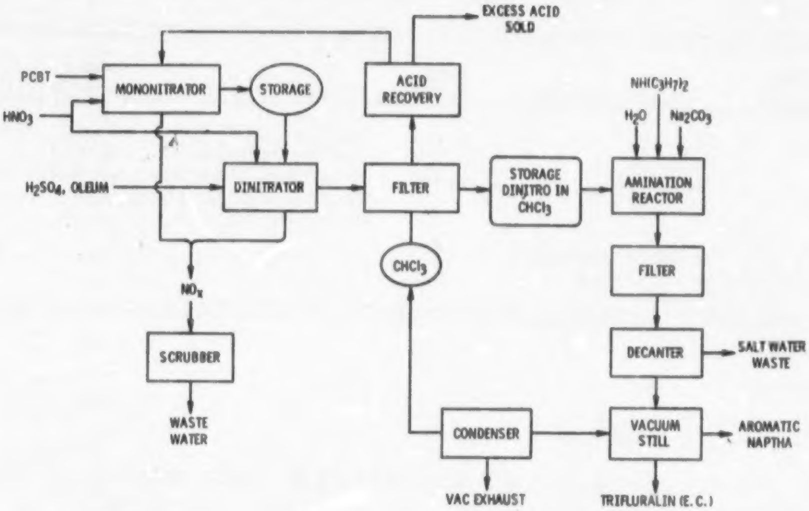

EXCESS ACID SOLD
PCBT
HNO_3
MONONITRATOR
STORAGE
ACID RECOVERY
$NH(C_3H_7)_2$
H_2O
Na_2CO_3
H_2SO_4, OLEUM
DINITRATOR
FILTER
STORAGE DINITRO IN $CHCl_3$
AMINATION REACTOR
$CHCl_3$
NO_x
FILTER
SCRUBBER
DECANTER
SALT WATER WASTE
WASTE WATER
CONDENSER
VACUUM STILL
AROMATIC NAPTHA
VAC EXHAUST
TRIFLURALIN (E. C.)

Figure 26. Production and waste handling schematic for trifluralin (13).

The main sources of air contaminant emissions are the nitration reactor and condenser. The main gaseous emissions from the nitration reactor are sulfur dioxide, sulfur trioxide, hydrogen fluoride, hydrogen chloride, and nitrogen oxides, while particulate emissions from the reactor consist of nitrate, sulfate, and chloride. Emissions from the condensers are mainly aerosol consisting of chloroform and trifluralin.

The raw materials used in the manufacture of trifluralin are nitric acid, sulfuric acid, sodium carbonate, dipropylamine, and *p*-chlorobenzotrifluoride. The main toxic materials are the acids, and their handling practices in chemical industries are well known.

Air contaminant emissions from the manufacture of trifluralin are both gases and particulates. The sole producer of trifluralin uses wet scrubbers for emissions control, their quoted efficiency being about 90% (13). Since aqueous waste from trifluralin manufacturing has been found to contain nitrosamines, dipropylnitrosamine could occur as an air emission. Table 25 lists several air contaminant emissions, sources, and rates from trifluralin manufacture (13).

TABLE 25. AIR CONTAMINANT EMISSIONS, SOURCES, AND RATES FROM TRIFLURALIN MANUFACTURE (13)

Manufacturing Process Source	Particulates	Rate, kg/hr	Gases/vapors	Rate, kg/hr	Odor	Rate, odor unit/hr
Nitration	Nitrate	0.454	Sulfur dioxide	1.36	None	–[a]
	Sulfate	0.454	Sulfur tioxide	0.454		
	Chloride	0.454	Hydrogen fluoride	0.454		
			Hydrogen chloride	1.36		
			Nitrogen oxides	1.36		
Condenser	Trichloromethane	–[a]	–[a]		None	–[a]
	Trifluralin	–[a]	–[a]			

[a] Not available.

Bacillus Thuringiensis

Bacillus thuringiensis, an insecticide (microbial product) containing crystalline toxin as the active ingredient, is produced by *bacillus thuringiensis* Berliner in the fermentation process shown below (12):

$$\text{Nutrient Mixture} \xrightarrow{\text{Sterilize}} \xrightarrow{\text{Innoculate}} \xrightarrow{\text{Ferment}}$$

$$\xrightarrow{\text{Separate}} \xrightarrow{\text{Dry}} \text{Solid containing} \sim 3\% \; B.t.$$

The production and waste schematic for *bacillus thuringiensis* is shown in Figure 27 (12). The fermentation process uses a nutrient mixture containing about 75% water in 37.8-m^3 to 132.5-m^3 tanks. The liquid mix is then sterilized and the sterile liquid is innoculated (1.9 x 10^{-2} m^3/37.8 m^3). The fermentation is submerged, proceeding aerobically as air is bubbled through for 2 to 3 days. During the process, temperature, pH, light, and stirring are regulated and turbidity is monitored.

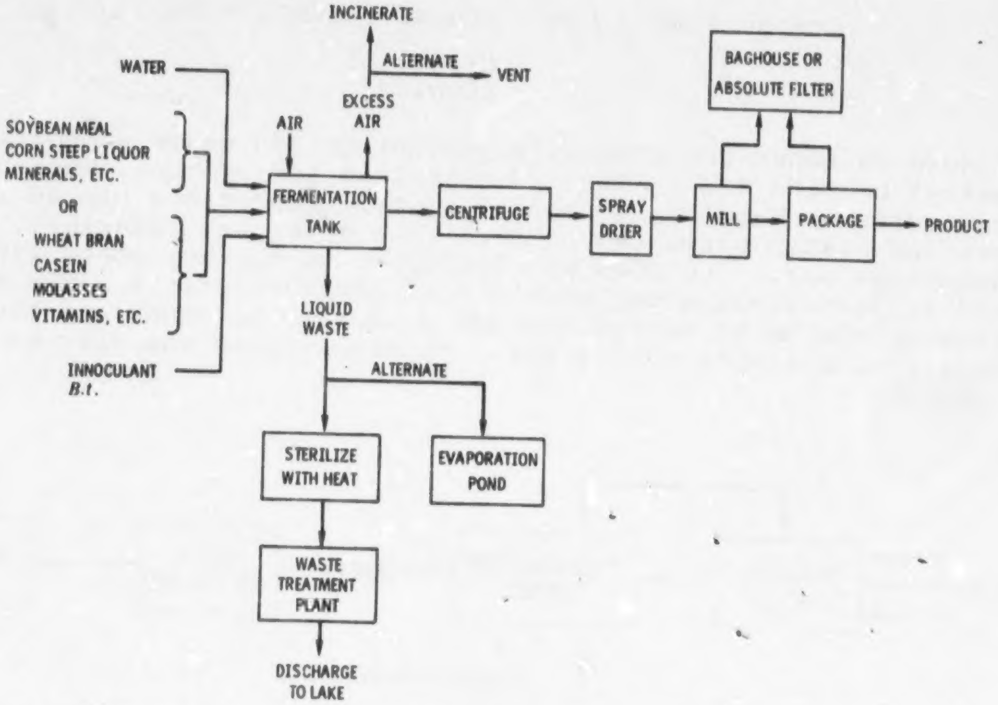

INCINERATE
ALTERNATE
VENT
WATER
EXCESS AIR
AIR
SOYBEAN MEAL
CORN STEEP LIQUOR
MINERALS, ETC.
OR
WHEAT BRAN
CASEIN
MOLASSES
VITAMINS, ETC.
INNOCULANT
B.t.
FERMENTATION TANK
CENTRIFUGE
SPRAY DRIER
MILL
PACKAGE
PRODUCT
BAGHOUSE OR ABSOLUTE FILTER
LIQUID WASTE
ALTERNATE
STERILIZE WITH HEAT
EVAPORATION POND
WASTE TREATMENT PLANT
DISCHARGE TO LAKE

Figure 27. Production and waste schematic for *bacillus thuringiensis* (12).

The product, a white milky suspension, is drained from the tank, centrifuged, and spray dried, and the powder is then milled and packaged (12).

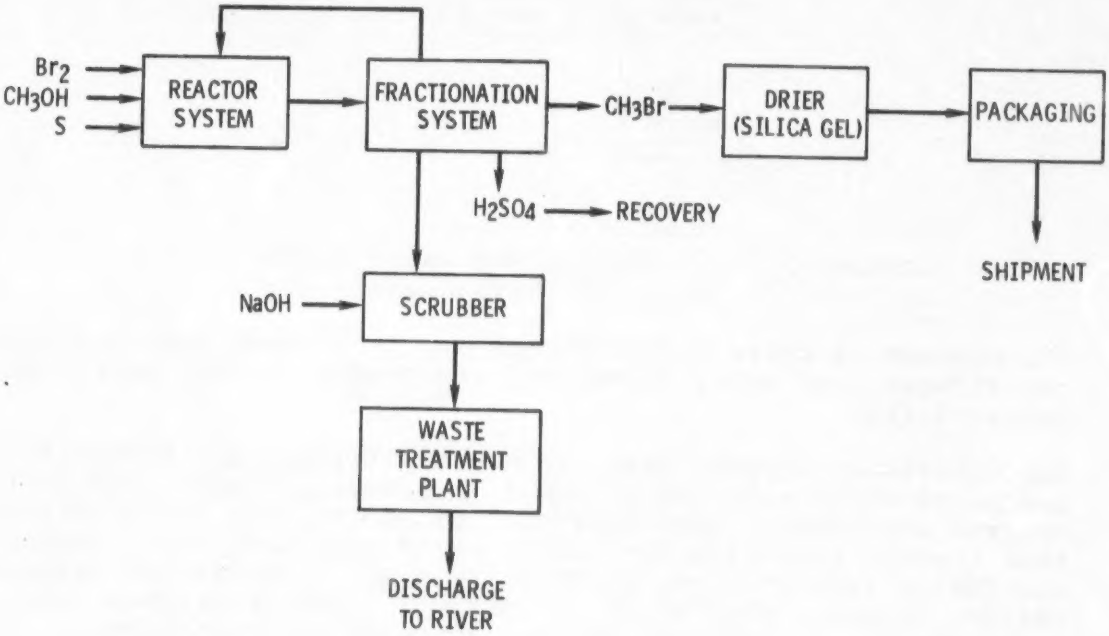
Raw materials (soybean meal, corn steep liquor, and minerals) are received by rail and unloaded in a shed equipped with dust control equipment. Materials are loaded into the fermentation tank through portholes with no reported dust problems. Excess air during fermentation, which may contain a variety of fermentation products, goes to an incinerator. The centrifuge and spray drier are contained so that no *bacillus thuringiensis* escapes to the atmosphere. The milling and packaging area is enclosed and maintained under negative pressure via vacuum takeoff through an absolute filter or baghouse, and the collected dust is recycled. One manufacturer maintains petri dish cultures throughout the plant to monitor for airborne biological emissions (12).

Methyl Bromide

Methyl bromide, classified in the "Other Pesticides" industry segment, is a highly toxic liquefied gas which is probably not persistent in sunlight. The production chemistry is as follows (15):

$$6CH_3OH + 3Br_2 + S \rightarrow \underset{\text{Methyl bromide}}{6CH_3Br} + H_2SO_4 + 2H_2O \qquad (28)$$

Figure 28 shows one company's production and waste schematic for methyl bromide (12). The raw materials are bromine, methanol and sulfur. Handling of methyl bromide requires a closed refrigeration system since the product is a colorless, odorless, poisonous gas. One possible byproduct is diethyl ether ($[CH_3]_2O$), and sulfur bromides may result from cross reactions. The methyl bromide system is vented through a caustic scrubber and the product is dried with silica gel. Emission rates and species are unknown.



Br_2
CH_3OH
S
REACTOR SYSTEM
FRACTIONATION SYSTEM
CH_3Br
DRIER (SILICA GEL)
PACKAGING
SHIPMENT
H_2SO_4
RECOVERY
NaOH
SCRUBBER
WASTE TREATMENT PLANT
DISCHARGE TO RIVER

Figure 28. Production and waste schematic for methyl bromide (12).

SECTION 6

PESTICIDE PRIORITIZATION

PRIORITIZATION MODEL

Prioritization listings developed for the Source Assessment Program have been used to aid in the selection of specific sources of emissions for detailed environmental assessment (18). Air pollution sources were rank ordered or prioritized by computing a relative environmental impact factor for each source type. A priority listing was thus developed for each of four industrial categories: combustion, organic materials, inorganic materials, and open sources. Pesticide chemical manufacturing source types received relatively low impact factors and thus a low rank compared to other organic and inorganic source types. This low rank, largely due to the smaller production of pesticides compared with other organic chemicals, is not representative of the potential environmental problem when one considers that pesticides are manufactured specifically to kill certain forms of life. In addition, a possibility of environmental contamination exists due to persistent pesticides which may be biologically accumulated in the food chain and which may produce long-term, low-level toxic effects on man.

Consequently, a new subcategory was formed to relatively rank pesticide chemical manufacturing source types, by pesticide chemical, with regard to their commonly described potential hazard to the environment from an air pollution standpoint. In this special project, pesticide source listings and a prioritization listing were produced specifically for use in evaluating pesticide manufacturing source types. A detailed description of the prioritization model and its development is given in Reference 18. The basic proposition of this model is that emission sources can be ranked, based upon the potential degree of hazard that they impose upon individuals in their environment. Factors used in the model include downwind concentration of emission species and an associated hazard factor, ambient air concentrations, ambient air quality standards, and population densities surrounding an emission source.

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(18) Eimutis, E. C. Source Assessment: Prioritization of Stationary Air Pollution Sources--Model Description. EPA-600/2-76-032a, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, February 1976. 77 pp.

The prioritization model generates an impact factor, I_x, associated with a given source type, x, and is defined as follows:

$$I_x = \sum_{j=1}^{K_x} P_j \left[\sum_{i=1}^{N} \left(\frac{\overline{\chi}_{ij}}{F_i} \right)^2 \frac{\chi'_{ij}}{S_i} \right]^{1/2} \tag{29}$$

where I_x = impact factor, person/km^2

K_x = number of sources emitting materials associated with source type x

N = number of materials emitted by each source

P_j = population density in the region associated with the jth source, persons/km^2

$\overline{\chi}_{ij}$ = calculated time-averaged maximum ground level concentration of the ith material emitted by the jth source, g/m^3

F_i = environmental hazard potential factor of the ith material, g/m^3

χ'_{ij} = ambient concentration of the ith material in the region associated with the jth source, g/m^3

S_i = corresponding standard for the ith material (used only for criteria emissions, otherwise set equal to one)

The values for the maximum time-averaged ground level concentration, $\overline{\chi}_{max}$, and hazard factor are defined as follows (18):

$$\overline{\chi}_{max} = \chi_{max} \left(\frac{t_o}{t_a} \right)^{0.17} \tag{30}$$

where $\chi_{max} = \frac{2\,Q}{\pi e u h^2}$ = instantaneous (i.e., 3-min average) maximum ground level concentration, g/m^3

t_o = instantaneous averaging time, 3 min

t_a = averaging time, min

Q = emission rate, g/s

h = stack height, m

π = 3.14

e = 2.72

u = wind speed, m/s

For criteria pollutants, the averaging time, t_a, is the same as that for the corresponding ambient air quality standard. For noncriteria emission species, t_a is 1,440 min (24 hr).

For the criteria pollutants--nitrogen oxides (NO_x), sulfur oxides (SO_x), carbon monoxide (CO), hydrocarbons, and particulates--F is the primary ambient air quality standard[a]. For other emission species, F is defined by a reduced TLV (19):

$$F = TLV\left(\frac{8}{24}\right)\left(\frac{1}{100}\right) \qquad (31)$$

where 8/24 normalizes the TLV to a 24-hr exposure and 1/100 is a safety factor.

PRIORITIZATION BY AIR EMISSIONS

A comprehensive assessment of the environmental significance of air emissions from pesticide manufacturing plants is inconceivable due to the limited quantitative emissions data available. The prioritization of major pesticide chemicals was conducted in order to give an indication of the relative significance of potential air emissions from these sources. Knowledge of simple process chemistry is not sufficient to qualify and quantify emissions because of the variations in production processes among plants. Detailed process information and production data are generally not available because this information is considered proprietary by manufacturers. Sources of emissions may vary from one production facility to another, and very little information is available concerning emission rates and species because few companies conduct in-house sampling programs.

The prioritization model is simply one tool used to aid in decision making regarding further characterization of the pesticide manufacturing industry. The pesticide ranking should by no means be considered rigid, but it should highlight areas for further consideration. For example, four of the highest ranked pesticides may be emitted from holding ponds or lagoons through evaporation. Their high rank is due primarily to the lack of data concerning evaporation emissions and to the fact that these pesticides may potentially impose a greater environmental burden than other source types. The impact factors generated by the prioritization model must not be taken out of context. Pesticide chemical manufacturing source types with impact factors in the

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[a] There is no primary ambient air quality standard for hydrocarbons. The value of 160 $\mu g/m^3$ used for hydrocarbons is a recommended guideline for meeting the primary ambient air quality standard for photochemical oxidants.

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(19) TLVs® Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1975. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1975. 97 pp.

upper 25% of the prioritization listing are likely to impose a greater environmental burden than those in the lower 25%.

The prioritization of 80 major pesticide chemical manufacturing source types gives a reasonable overview of the pesticide manufacturing industry. In 1974, 37 major organic pesticides accounted for 74% (4.72 x 10^5 metric tons) of the total production (2). The remaining 26% of production was divided among some 300 other synthetic organic pesticides, and only about one-third of these had production greater than 454 metric tons. This prioritization covers an estimated 81% (5.2 x 10^5 metric tons) of total synthetic organic pesticide production based on 1974 estimates. Certain industrial chemicals with minor pesticide uses, shown in Table 26, were excluded from this prioritization because they are primarily products of other industries and are predominantly used for other purposes.

TABLE 26. INDUSTRIAL CHEMICALS, USEFUL AS PESTICIDES, EXCLUDED FROM THE PESTICIDE PRIORITIZATION

Acrolein
Acrylonitrile
Allyl alcohol
Ammonium thiocyanate
Anthraquinone
Arsenic acid
Biphenyl
Bis(diethylthiocarbamoyl)disulfide
Bis(dimethylthiocarbamoyl)disulfide
Bis(dimethylthiocarbamoyl)sulfide

Borascu
Borax } Sodium borates
Boro-Spray
Carbon disulfide
Carbon tetrachloride
Copper acetoarsenite (Paris Green)
Copper carbonate
Copper naphthenate
Copper oleate
Copper oxychloride sulfate
Copper sulfate

DHA (dehydroacetic acid)
DMP (dimethyl phthalate)
Dichlorobenzene (*ortho* and *para* isomers)
Dimethyldithiocarbamic acid, K salt
Dimethyldithiocarbamic acid, Na salt
Dimethyldithiocarbamic acid, Zn salt
Diphenylamine
Ethylene
Ethylene dibromide
Ethylene dibromide
Ethylene dichloride
Ethylene oxide
Ethyl formate
Formaldehyde, formalin
HCN (hydrocyanic acid)
Mercuric chloride
OPP (*o*-phenylphenol)
Sodium arsenite
Sodium chlorate
Sodium fluoride
Sulfur
Thiram

The prioritization listing for 80 source types, compiled from the emissions data summarized in Appendix B, is presented in Table 27. The column labeled UL is the uncertainty level designation that is discussed later in Section 6.

As noted earlier, this prioritization should highlight areas where there is a high potential environmental burden or where key

TABLE 27. PRIORITIZATION OF PESTICIDE CHEMICAL MANUFACTURING SOURCES WITH RESPECT TO SOURCE TYPE

SOURCE TYPE	IMPACT FACTOR	UL	CALC
TOXAPHENE	300,000	C	3
PHORATE	70,000	D	3
METHOXYCHLOR	40,000	D	3
DIAZINON	30,000	D	3
MANEB	10,000	D	3
ZINEB	7,000	D	3
DDT	7,000	D	3
METHYL PARATHION	6,000	B	3
PARATHION	5,000	B	3
DICOFOL	4,000	D	3
MALATHION	4,000	C	3
MONOCROTOPHOS	3,000	D	3
PENTACHLOROPHENOL AND SODIUM SALTS	2,000	B	3
CARBOFURAN	2,000	D	3
DISULFOTON	2,000	D	3
2,4-D ACID, ESTERS, SALTS	2,000	D	3
AZINOPHOS - ETHYL	1,000	D	3
FENSULFOTHION	1,000	D	3
BROMACIL	1,000	D	3
CHLORDANE	1,000	D	3
TRICHLOROPHENOLS	1,000	C	3
CARBARYL	900	D	3
NABAM	900	D	3
ALDICARB	800	D	3
PROPANIL	800	D	3
DBCP	800	D	3
DIMETHOATE	700	C	3
CHLORAMBEN	600	D	3
FLUOMETURON	500	D	3
NALED	500	D	3
HEXACHLOROBENZENE	400	D	3
DICROTOPHOS	400	D	3
AZINOPHOS - METHYL	400	D	3
MSMA	400	B	3
TRIFLURALIN	300	B	3
MEVINPHOS	300	D	3
METHYL BROMIDE	200	D	3
CHLORPYRIFOS	200	D	3
DIURON	200	D	3
DICHLOROVOS	200	D	3
BUTYLATE	100	D	3
DSMA	100	B	3
EPTC	100	D	3
PHOSPHAMIDION	100	D	3
DICHLOROPROPENE	90	D	3
TERBACIL	90	D	3
DALAPON	80	D	3
SILVEX	80	D	3
LINDANE	70	D	3
VERNOLATE	60	D	3
MERPHOS	60	D	3
PYRETHINS	50	D	3
METALKAMATE (BUX)	50	D	3
DICAMBA	50	D	3
LINURON	50	D	3
RENEFIN	40	D	3
CAPTAN	40	B	3
ATRAZINE	40	D	3
DINOSEB	30	C	3
TEPP	30	D	3
ENDRIN	30	D	3
HEPTACHLOR	30	D	3
ENDOSULFAN	20	D	3
MONURON	20	D	3
SODIUM TCA	20	D	3
RONNEL	20	D	3
CDEC	7	D	3
CACODYLIC ACID	6	D	3
SIMAZINE	5	D	3
FOLPET	5	E	3
PROPACHLOR	4	D	3
PROPAZINE	4	D	3
BACILLUS THURINGIENSIS	3	D	3
BUTACHLOR	2	D	3
CAPTAFOL	2	C	3
ALACHLOR	1	D	3
CALCIUM ACID METHANEARSONATE		D	3
CALCIUM ARSENATE		D	3
LEAD ARSENATE		D	3
METHANE ARSENIC ACID		D	3

information is lacking. A close look at several pesticides with the highest impact factors highlights two facts: 1) no information is available concerning the environmental burden due to potential evaporation emissions from holding ponds and evaporation lagoons and 2) sulfur dioxide emissions may be substantial for some pesticides due to the flaring of H_2S and mercaptans and the incineration of sulfur-containing compounds.

Four pesticides (toxaphene, DDT, methyl parathion, and parathion) out of the nine pesticides with the highest impact factors are each potentially emitted to the atmosphere from holding ponds or lagoons. Emission factors for evaporation of these compounds were calculated using the methodology presented in Appendix A. Eight pesticides (phorate, diazinon, maneb, zineb, methyl parathion, parathion, malathion, and monocrotophos) appear in the upper 20% of the prioritization list due primarily to the potentially high emission of SO_2 resulting from flaring H_2S and mercaptans and from incineration of sulfur-containing compounds. Methoxychlor received a large impact factor primarily due to the high county population densities associated with its manufacturing sites.

Methyl parathion and parathion are also ranked in the upper portion of the prioritization listing, primarily due to the emission of SO_2, a result of flaring H_2S and mercaptans and incinerating sulfur. H_2S byproduct has been calculated as 0.12 kg/kg of active ingredient (12). Sulfur dioxide emission rates, based on H_2S and S oxidation, are estimated to be 704 kg/hr (13) or 0.41 kg SO_2/kg active ingredient (2). Potential emissions from wastewater treatment or lagooning include the pesticides, ammonia (the emission factor for pesticides and ammonia is calculated using the methodology in Appendix A), mercaptans and H_2S.

Disulfoton, phorate, fensulfothion, diazinon, dursban, and merphos were all assumed to have the same SO_2 emission factor based on their similarities and the fact that 0.06 kg H_2S/kg active ingredient is produced as a reaction byproduct during the manufacture of disulfoton (12). Based on sulfur dioxide emission rates calculated for methyl parathion and parathion (H_2S byproduct formation was calculated as 0.12 kg/kg active ingredient), the SO_2 emission factor is estimated to be 0.2 kg SO_2/kg active ingredient or 205 kg/metric ton.

It is also noted that atrazine, the largest selling herbicide in the United States, and captan, with an estimated annual production of 9.1×10^3 metric tons, are ranked in the lower half of the prioritization due to lack of information on which to base better qualified emission estimates. In general, the existence of any compound in the lower half of the prioritization list may well be due to a lack of emissions data.

MASS OF EMISSIONS

State-by-state and national listings refer to a compilation of mass emissions of criteria pollutants (particulates, SO_x [reported as SO_2], NO_x, hydrocarbons [designated HC], and CO) by pesticide source type for specific states and for the nation. The total mass of emissions of a specific criteria pollutant in a particular state was obtained by multiplying the pollutant emission factor (Appendix B) by the annual production rate in the state. Similarly, the total mass of emissions of a criteria pollutant in the nation was obtained by multiplying the pollutant emission factor by the annual total production in the United States (Table 4).

State-by-State Listing

The state-by-state listing of criteria pollutant emissions from pesticide manufacturing source types is given in Table 28. This listing shows the pesticide chemical manufacturing source types in a particular state that emit one or more of the criteria pollutants. The first number in each criteria pollutant column is the annual mass of that emission in the particular state. For example, the source type entitled "Butylate" emits 0.9×10^3 kg/yr of particulates in Alabama. The second number in each criteria pollutant column refers to the percentage that the annual mass of emissions represents in relation to the total emissions of that pollutant from all pesticide chemical manufacturing source types in that state. For the same source type, "Butylate," in Alabama, 0.9×10^3 kg/yr represent 4.21% of all particulates emitted from all pesticide chemical manufacturing sources in Alabama.

National Listing

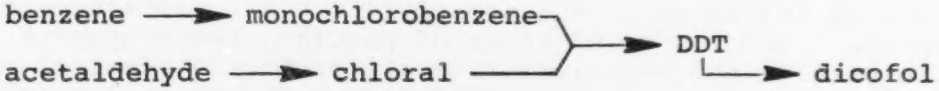
The national listing of criteria pollutant emissions from pesticide chemical manufacturing source types is shown in Table 29. For each source type and each criteria pollutant, the first line represents the annual mass of emissions of each pollutant from each source type. For example, the source type "Butylate" accounts for 1.8×10^3 kg/yr of particulate emissions in the United States. The percentage of emissions which a source type represents with respect to all pesticide chemical manufacturing sources is indicated on the second line. For the source type "Butylate," the 1.8×10^3 kg/yr of particulates represent 0.85% of the particulate emissions from all pesticide chemical manufacturing sources in the United States. The third line shows the percent of emissions from all sources of air emissions in the United States represented by this same source type. In the case of butylate, as well as the majority of source types, the percentage is too low to be represented by the given number of decimal places. However, the butylate source does produce 743.9×10^3 kg/yr of sulfur oxide emissions (reported as SO_2) which represent 0.00115% of the SO_2 emissions from all sources in the United States. In addition, dashes in a criteria pollutant column (for example, the calcium arsenate source type) indicate that the combined mass of emissions for the particular source type is not significant to the given number of five decimal places.

DATA SOURCES, QUALITY, AND METHODOLOGY

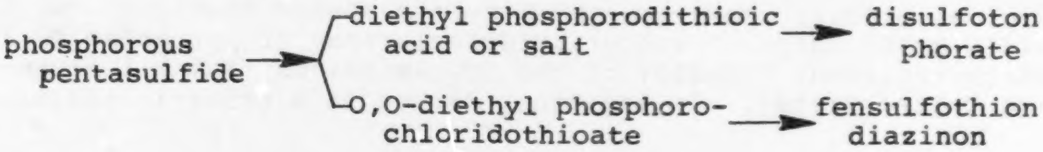
Available information regarding principal emission species and emission rates is listed in Table 22 for seven major pesticides. Three of these compounds are included in the chlorinated hydrocarbons industry segment, and one is included in each of four other industrial segments: organophosphates, organoarsenicals and organometallics, nitrated hydrocarbons, and other nitrogenous hydrocarbons. The calculated emission estimates in Table 22 were used as a basis to derive emission factor estimates for the remaining pesticides within each industry segment. Additional input used for organophosphorus pesticides includes: 208.8 kg/hr hydrogen chloride and 190.7 kg/hr sulfur from the methyl parathion chlorination unit prior to incineration and flaring. Sulfur dioxide emission rates based on H_2S and S oxidation from incineration and flaring are estimated to be 703.7 kg/hr.

For prioritization purposes, several assumptions were made. Provided that similar assumptions are made throughout the prioritization, no added weight would be given to any single pesticide or industry segment (e.g., organophosphates). For example, detailed information on emission height is not available; therefore, a constant emission height of 30.5 m was assumed throughout the prioritization. Due to the lack of quantitative emission height data, this value was estimated and provided no added weight to any source type. The prioritization is thus composed of consistent estimates based on available data and similarities between pesticide manufacturing processes, raw materials utilized, and chemical structures.

In certain cases, similarities between pesticides are present, and their emission estimates are thus assumed to be similar. For example, dicofol was assumed to have emissions similar to those of DDT. Dicofol production may be represented by the following flow diagram:



Similarly, disulfoton, phorate, fensulfothion and diazinon were all given similar emission estimates based on the following diagram:


phosphorous pentasulfide
diethyl phosphorodithioic acid or salt
disulfoton
phorate
O,O-diethyl phosphorochloridothioate
fensulfothion
diazinon

Emission factors derived using this methodology should provide sufficient information to develop the prioritization, although uncertainty is associated with the emission estimates for each source type. While the level of uncertainly cannot be quantified, it can be assumed to vary as a function of the guality of available information on a specific pesticide. Using this rationale, a priority index of uncertainty levels may be defined as follows:

Level	Meaning
A	Adequate data of reasonable accuracy
B	Partially estimated data of intermediate accuracy
C	Totally estimated data of intermediate accuracy
D	Missing data and unknown emission species

The above defined uncertainty levels are subjective. They ranged from B to D for the source types in this prioritization. The pesticides listed in Table 22, in addition to DSMA and parathion and excluding toxaphene, were assigned a confidence level of B. Captafol, dimethoate, dinoseb, folpet, malathion, toxaphene, and trichlorophenols were assigned a confidence level of C, while the remaining pesticides were assigned a D level of uncertainty.

TABLE 28. STATE-BY-STATE LISTING OF CRITERIA POLLUTANT EMISSIONS FROM PRIORITIZED PESTICIDE CHEMICAL MANUFACTURING SOURCES

STATE EMISSIONS REPORT FOR ALABAMA[a]

```
                                         MASS OF EMISSIONS (1000 KG/YR)
                                         PERCENT OF STATE EMISSIONS

   SOURCE                     PART        SO2        NOX         HC          CO     T
   ------                     ----        ---        ---         --          --     -

  BUTYLATE                     0.9      372.0        0.0        2.7         0.0    2
                           4.21000    4.26000    0.00000    9.56000     0.00000

  DBCP                         0.0        0.0        0.0        2.7         0.0    2
                           0.00000    0.00000    0.00000    9.56000     0.00000

  DIAZINON                     1.4      557.9        0.0        0.0         0.0    2
                           6.32000    6.38000    0.00000    0.00000     0.00000

  DICHLOROVOS                  0.1        0.0        0.0        0.2         0.0    2
                           0.42100    0.00000    0.00000    0.63700     0.00000

  EPTC                         0.7      279.0        0.0        2.0         0.0    2
                           3.16000    3.19000    0.00000    7.17000     0.00000

  METHYL PARATHION            13.6     5579.0        0.0       13.6         0.0    2
                          63.20000   63.80000    0.00000   47.80000     0.00000

  MEVINPHOS                    0.1        0.0        0.0        0.1         0.0    2
                           0.52700    0.00000    0.00000    0.39800     0.00000

  PARATHION                    3.6     1488.0        0.0        3.7         0.0    2
                          16.90000   17.00000    0.00000   12.90000     0.00000

  VERNOLATE                    1.1      464.9        0.0        3.4         0.0    2
                           5.27000    5.32000    0.00000   11.90000     0.00000


  STATE TOTALS                21.5     8741.0        0.0       28.5         0.0
```

STATE EMISSIONS REPORT FOR ALASKA

```
                                         MASS OF EMISSIONS (1000 KG/YR)
                                         PERCENT OF STATE EMISSIONS

   SOURCE                     PART        SO2        NOX         HC          CO     T
   ------                     ----        ---        ---         --          --     -
```

(continued)

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[a] Producers and plant locations were derived from Reference 2. It must be qualified that certain prioritized pesticides may not be listed in state emission report due to the limited quality of data concerning pesticide manufacturer locations.

TABLE 28 (continued)

STATE EMISSIONS REPORT FOR ARIZONA

SOURCE	PART	SO2	NOX	HC	CO	T
	MASS OF EMISSIONS (1000 KG/YR) PERCENT OF STATE EMISSIONS					

STATE EMISSIONS REPORT FOR ARKANSAS

SOURCE	PART	SO2	NOX	HC	CO	T
	MASS OF EMISSIONS (1000 KG/YR) PERCENT OF STATE EMISSIONS					
2,4-D ACID, ESTERS, SALTS	2.3 42.00000	0.0 0.00000	0.0 0.00000	2.3 22.10000	0.0 0.00000	2
DALAPON	0.6 10.50000	0.0 0.00000	0.0 0.00000	0.6 5.53000	0.0 0.00000	2
METHYL BROMIDE	0.0 0.00000	0.0 0.00000	0.0 0.00000	2.3 22.10000	0.0 0.00000	2
SILVEX	0.7 12.60000	0.0 0.00000	0.0 0.00000	1.4 13.30000	0.0 0.00000	2
TRICHLOROPHENOLS	1.9 35.00000	0.0 0.00000	0.0 0.00000	3.8 36.90000	0.0 0.00000	2
STATE TOTALS	5.4	0.0	0.0	10.2	0.0	

(continued)

TABLE 28 (continued)

STATE EMISSIONS REPORT FOR CALIFORNIA

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T
BACILLUS THURINGIENSIS	0.2 1.39000	0.0 0.00000	0.0 0.00000	0.0 0.00000	0.0 0.00000	2
CAPTAFOL	0.1 0.54900	0.0 0.00000	0.0 0.00000	1.4 4.26000	0.0 0.00000	2
2,4-D ACID, ESTERS, SALTS	2.3 13.90000	0.0 0.00000	0.0 0.00000	2.3 7.11000	0.0 0.00000	2
DDT	13.6 83.20000	0.0 0.00000	0.0 0.00000	27.2 85.30000	0.0 0.00000	2
METHYL BROMIDE	0.0 0.00000	0.0 0.00000	0.0 0.00000	0.9 2.84000	0.0 0.00000	2
NALED	0.1 0.69400	0.0 0.00000	0.0 0.00000	0.1 0.35500	0.0 0.00000	2
PHOSPHAMIDION	0.0 0.27700	0.0 0.00000	0.0 0.00000	0.0 0.14200	0.0 0.00000	2
STATE TOTALS	16.3	0.0	0.0	31.9	0.0	

(continued)

TABLE 28 (continued)

STATE EMISSIONS REPORT FOR COLORADO

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T
DBCP	0.0 0.00000	0.0 0.00000	0.0 0.00000	2.7 56.90000	0.0 0.00000	2
DICHLOROVOS	0.1 4.60000	0.0 0.00000	0.0 0.00000	0.2 3.79000	0.0 0.00000	2
DICROTOPHOS	0.2 9.20000	0.0 0.00000	0.0 0.00000	0.2 3.79000	0.0 0.00000	2
MEVINPHOS	0.1 5.75000	0.0 0.00000	0.0 0.00000	0.1 2.37000	0.0 0.00000	2
MONOCROTOPHOS	1.6 80.50000	0.0 0.00000	0.0 0.00000	1.6 33.20000	0.0 0.00000	2
STATE TOTALS	2.0	0.0	0.0	4.8	0.0	

STATE EMISSIONS REPORT FOR CONNECTICUT

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T
CAPTAN	0.2 9.54000	0.0 0.00000	0.0 0.00000	3.0 44.40000	0.0 0.00000	2
TRICHLOROPHENOLS	1.9 90.50000	0.0 0.00000	0.0 0.00000	3.8 55.60000	0.0 0.00000	2
STATE TOTALS	2.1	0.0	0.0	6.8	0.0	

(continued)

TABLE 28 (continued)

STATE EMISSIONS REPORT FOR DELAWARE

SOURCE	PART	SO2	NOX	HC	CO	T
	MASS OF EMISSIONS (1000 KG/YR) PERCENT OF STATE EMISSIONS					

STATE EMISSIONS REPORT FOR FLORIDA

SOURCE	PART	SO2	NOX	HC	CO	T
	MASS OF EMISSIONS (1000 KG/YR) PERCENT OF STATE EMISSIONS					
NALED	0.1 71.40000	0.0 0.00000	0.0 0.00000	0.1 71.40000	0.0 0.00000	2
PHOSPHAMIDION	0.0 28.60000	0.0 0.00000	0.0 0.00000	0.0 28.60000	0.0 0.00000	2
STATE TOTALS	0.2	0.0	0.0	0.2	0.0	

STATE EMISSIONS REPORT FOR GEORGIA

SOURCE	PART	SO2	NOX	HC	CO	T
	MASS OF EMISSIONS (1000 KG/YR) PERCENT OF STATE EMISSIONS					
CALCIUM ARSENATE	0.0 0.00086	0.0 0.00000	0.0 0.00000	0.0 0.00000	0.0 0.00000	2
LEAD ARSENATE	0.0 0.00571	0.0 0.00000	0.0 0.00000	0.0 0.00000	0.0 0.00000	2
TOXAPHENE	0.0 100.00000	0.0 0.00000	0.0 0.00000	40.6 100.00000	0.0 0.00000	2
STATE TOTALS	0.0	0.0	0.0	40.6	0.0	

(continued)

TABLE 28 (continued)

STATE EMISSIONS REPORT FOR HAWAII

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T

STATE EMISSIONS REPORT FOR IDAHO

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T

STATE EMISSIONS REPORT FOR ILLINOIS

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T
BACILLUS THURINGIENSIS	0.2 1.52000	0.0 0.00000	0.0 0.00000	0.0 0.00000	0.0 0.00000	2
CHLORDANE	0.0 0.00000	0.0 0.00000	0.0 0.00000	3.4 31.60000	0.0 0.00000	2
2,4-D ACID, ESTERS, SALTS	2.3 15.20000	0.0 0.00000	0.0 0.00000	2.3 21.10000	0.0 0.00000	2
FLUOMETURON	0.0 0.00000	0.0 0.00000	0.0 0.00000	0.6 5.26000	0.0 0.00000	2
PENTACHLOROPHENOL AND SODIUM SALTS	12.5 83.30000	0.0 0.00000	0.0 0.00000	4.5 42.10000	0.0 0.00000	2
STATE TOTALS	15.0	0.0	0.0	10.8	0.0	

(continued)

TABLE 28 (continued)

STATE EMISSIONS REPORT FOR INDIANA

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T
BENEFIN	1.3	1.7	1.3	0.0	0.0	2
	10.70000	10.70000	10.70000	0.00000	0.00000	
TRIFLURALIN	10.9	14.5	10.9	0.0	0.0	2
	89.30000	89.30000	89.30000	0.00000	0.00000	
STATE TOTALS	12.2	16.3	12.2	0.0	0.0	

STATE EMISSIONS REPORT FOR IOWA

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T
ALACHLOR	0.0	0.0	0.0	0.3	0.0	2
	0.00000	0.00000	0.00000	1.13000	0.00000	
BUTACHLOR	0.0	0.0	0.0	6.8	0.0	2
	0.00000	0.00000	0.00000	28.20000	0.00000	
METALKAMATE (BUX)	2.3	0.0	0.0	6.8	0.0	2
	100.00000	0.00000	0.00000	28.20000	0.00000	
PROPACHLOR	0.0	0.0	0.0	10.2	0.0	2
	0.00000	0.00000	0.00000	42.40000	0.00000	
STATE TOTALS	2.3	0.0	0.0	24.1	0.0	

STATE EMISSIONS REPORT FOR KANSAS

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T
DIMETHOATE	0.3	0.2	0.2	1.4	0.0	2
	1.49000	100.00000	100.00000	14.30000	0.00000	
PENTACHLOROPHENOL AND SODIUM SALTS	22.4	0.0	0.0	8.2	0.0	2
	98.50000	0.00000	0.00000	85.70000	0.00000	
STATE TOTALS	22.8	0.2	0.2	9.5	0.0	

(continued)

TABLE 28 (continued)
STATE EMISSIONS REPORT FOR KENTUCKY

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T
2,4-D ACID, ESTERS, SALTS	4.5 100.00000	0.0 0.00000	0.0 0.00000	4.5 100.00000	0.0 0.00000	2
STATE TOTALS	4.5	0.0	0.0	4.5	0.0	

STATE EMISSIONS REPORT FOR LOUISIANA

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T
ATRAZINE	0.0 0.00000	0.0 0.00000	0.0 0.00000	74.8 72.60000	0.0 0.00000	2
BUTYLATE	0.9 23.50000	372.0 57.10000	0.0 0.00000	2.7 2.64000	0.0 0.00000	2
2,4-D ACID, ESTERS, SALTS	2.3 58.80000	0.0 0.00000	0.0 0.00000	2.3 2.20000	0.0 0.00000	2
DICHLOROPROPENE	0.0 0.00000	0.0 0.00000	0.0 0.00000	3.6 3.52000	0.0 0.00000	2
EPTC	0.7 17.60000	279.0 42.90000	0.0 0.00000	2.0 1.98000	0.0 0.00000	2
FLUOMETURON	0.0 0.00000	0.0 0.00000	0.0 0.00000	0.6 0.55000	0.0 0.00000	2
PROPAZINE	0.0 0.00000	0.0 0.00000	0.0 0.00000	6.8 6.60000	0.0 0.00000	2
SIMAZINE	0.0 0.00000	0.0 0.00000	0.0 0.00000	10.2 9.90000	0.0 0.00000	2
STATE TOTALS	3.9	650.9	0.0	103.1	0.0	

STATE EMISSIONS REPORT FOR MAINE

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T

(continued)

TABLE 28 (continued)

STATE EMISSIONS REPORT FOR MARYLAND

SOURCE	MASS OF EMISSIONS (1000 KG/YR) PERCENT OF STATE EMISSIONS PART	 SO2	 NOX	 HC	 CO	 T
AZINOPHOS - ETHYL	0.7 83.30000	0.2 100.00000	0.2 100.00000	1.0 88.20000	0.0 0.00000	2
PYRETHINS	0.1 16.70000	0.0 0.00000	0.0 0.00000	0.1 11.80000	0.0 0.00000	2
STATE TOTALS	0.8	0.2	0.2	1.2	0.0	

STATE EMISSIONS REPORT FOR MASSACHUSETTS

SOURCE	MASS OF EMISSIONS (1000 KG/YR) PERCENT OF STATE EMISSIONS PART	 SO2	 NOX	 HC	 CO	 T

(continued)

TABLE 28 (continued)
STATE EMISSIONS REPORT FOR MICHIGAN

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T
CHLORPYRIFOS	1.1 5.78000	464.9 74.00000	0.0 0.00000	0.0 0.00000	0.0 0.00000	2
2,4-D ACID, ESTERS, SALTS	2.3 11.60000	0.0 0.00000	0.0 0.00000	2.3 7.85000	0.0 0.00000	2
DALAPON	0.6 2.89000	0.0 0.00000	0.0 0.00000	0.6 1.96000	0.0 0.00000	2
DBCP	0.0 0.00000	0.0 0.00000	0.0 0.00000	3.6 12.60000	0.0 0.00000	2
DINOSEB	0.4 2.22000	0.6 0.09240	0.4 64.00000	0.5 1.57000	0.0 0.00000	2
METHYL BROMIDE	0.0 0.00000	0.0 0.00000	0.0 0.00000	3.9 13.30000	0.0 0.00000	2
PENTACHLOROPHENOL AND SODIUM SALTS	12.5 63.60000	0.0 0.00000	0.0 0.00000	4.5 15.70000	0.0 0.00000	2
RONNEL	0.5 2.31000	0.3 0.04620	0.2 36.00000	1.8 6.28000	0.0 0.00000	2
SODIUM TCA	0.0 0.00000	0.0 0.00000	0.0 0.00000	6.8 23.50000	0.0 0.00000	2
TRICHLOROPHENOLS	1.9 9.68000	0.0 0.00000	0.0 0.00000	3.8 13.10000	0.0 0.00000	2
ZINEB	0.4 2.02000	162.7 25.90000	0.0 0.00000	1.2 4.12000	0.0 0.00000	2
STATE TOTALS	19.6	628.5	0.7	28.9	0.0	

STATE EMISSIONS REPORT FOR MINNESOTA

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T
PYRETHINS	0.1 100.00000	0.0 0.00000	0.0 0.00000	0.1 100.00000	0.0 0.00000	2
STATE TOTALS	0.1	0.0	0.0	0.1	0.0	

(continued)

TABLE 28 (continued)

STATE EMISSIONS REPORT FOR MISSISSIPPI

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T
DINOSEB	0.4 6.88000	0.6 0.02400	0.4 100.00000	0.5 2.52000	0.0 0.00000	2
METHYL PARATHION	4.5 71.60000	1860.0 76.90000	0.0 0.00000	4.5 25.20000	0.0 0.00000	2
PARATHION	1.4 21.50000	557.9 23.10000	0.0 0.00000	1.4 7.67000	0.0 0.00000	2
TOXAPHENE	0.0 0.00072	0.0 0.00000	0.0 0.00000	11.6 64.60000	0.0 0.00000	2
STATE TOTALS	6.3	2418.0	0.4	18.0	0.0	

STATE EMISSIONS REPORT FOR MISSOURI

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T
AZINOPHOS - METHYL	0.9 13.00000	0.3 0.01950	0.2 100.00000	1.4 35.90000	0.0 0.00000	2
2,4-D ACID, ESTERS, SALTS	2.3 32.60000	0.0 0.00000	0.0 0.00000	2.3 59.90000	0.0 0.00000	2
DISULFOTON	2.3 32.60000	929.9 62.50000	0.0 0.00000	0.0 0.00000	0.0 0.00000	2
FENSULFOTHION	1.4 19.50000	557.9 37.50000	0.0 0.00000	0.0 0.00000	0.0 0.00000	2
NALED	0.1 1.63000	0.0 0.00000	0.0 0.00000	0.1 2.99000	0.0 0.00000	2
PHOSPHAMIDION	0.0 0.65100	0.0 0.00000	0.0 0.00000	0.0 1.20000	0.0 0.00000	2
STATE TOTALS	7.0	1488.0	0.2	3.8	0.0	

(continued)

TABLE 28 (continued)

STATE EMISSIONS REPORT FOR MONTANA

SOURCE		MASS OF EMISSIONS (1000 KG/YR) PERCENT OF STATE EMISSIONS				
	PART	SO2	NOX	HC	CO	T

STATE EMISSIONS REPORT FOR NEBRASKA

SOURCE		MASS OF EMISSIONS (1000 KG/YR) PERCENT OF STATE EMISSIONS				
	PART	SO2	NOX	HC	CO	T

STATE EMISSIONS REPORT FOR NEVADA

SOURCE		MASS OF EMISSIONS (1000 KG/YR) PERCENT OF STATE EMISSIONS				
	PART	SO2	NOX	HC	CO	T

STATE EMISSIONS REPORT FOR NEW HAMPSHIRE

SOURCE		MASS OF EMISSIONS (1000 KG/YR) PERCENT OF STATE EMISSIONS				
	PART	SO2	NOX	HC	CO	T

(continued)

TABLE 28 (continued)

STATE EMISSIONS REPORT FOR NEW JERSEY

SOURCE	MASS OF EMISSIONS (1000 KG/YR) PERCENT OF STATE EMISSIONS PART	 SO2	 NOX	 HC	 CO	 T
CACODYLIC ACID	0.0 0.00000	0.0 0.00000	0.0 0.00000	0.8 1.14000	0.0 0.00000	2
CHLORDANE	0.0 0.00000	0.0 0.00000	0.0 0.00000	3.4 4.97000	0.0 0.00000	2
DIAZINON	1.4 9.06000	557.9 24.70000	0.0 0.00000	0.0 0.00000	0.0 0.00000	2
DIMETHOATE	0.3 2.26000	0.2 0.00963	0.2 4.28000	1.4 1.99000	0.0 0.00000	2
DINOSEB	0.4 2.90000	0.6 0.02570	0.4 10.10000	0.5 0.66200	0.0 0.00000	2
DSMA	0.0 0.00000	0.0 0.00000	0.0 0.00000	2.6 3.81000	0.0 0.00000	2
HEXACHLOROBENZENE	0.0 0.00000	0.0 0.00000	0.0 0.00000	1.8 2.65000	0.0 0.00000	2
LINDANE	0.0 0.00000	0.0 0.00000	0.0 0.00000	0.5 0.66200	0.0 0.00000	2
MALATHION	6.8 45.30000	4.4 0.19800	3.7 85.60000	27.2 39.70000	0.0 0.00000	2
MANEB	0.9 6.04000	372.0 16.50000	0.0 0.00000	2.7 3.97000	0.0 0.00000	2
METHOXYCHLOR	1.5 10.10000	0.0 0.00000	0.0 0.00000	1.5 2.21000	0.0 0.00000	2
MSMA	0.0 0.00000	0.0 0.00000	0.0 0.00000	9.0 13.10000	0.0 0.00000	2
NABAM	0.6 3.77000	232.5 10.30000	0.0 0.00000	1.7 2.48000	0.0 0.00000	2
NALED	0.1 0.75500	0.0 0.00000	0.0 0.00000	0.1 0.16600	0.0 0.00000	2
PHORATE	2.3 15.10000	929.9 41.10000	0.0 0.00000	0.0 0.00000	0.0 0.00000	2
PHOSPHAMIDION	0.0 0.30200	0.0 0.00000	0.0 0.00000	0.0 0.06620	0.0 0.00000	2
PROPANIL	0.0 0.00000	0.0 0.00000	0.0 0.00000	2.3 3.31000	0.0 0.00000	2
PYRETHINS	0.3 1.81000	0.0 0.00000	0.0 0.00000	0.3 0.39700	0.0 0.00000	2
TOXAPHENE	0.0 0.00030	0.0 0.00000	0.0 0.00000	11.6 17.00000	0.0 0.00000	2
ZINEB	0.4 2.64000	162.7 7.20000	0.0 0.00000	1.2 1.74000	0.0 0.00000	2
STATE TOTALS	15.0	2260.0	4.3	68.5	0.0	

(continued)

TABLE 28 (continued)

STATE EMISSIONS REPORT FOR NEW MEXICO

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T

STATE EMISSIONS REPORT FOR NEW YORK

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T
CARBOFURAN	1.1 74.10000	0.0 0.00000	0.0 0.00000	3.4 43.80000	0.0 0.00000	2
ENDOSULFAN	0.0 0.00000	0.0 0.00000	0.0 0.00000	1.4 17.50000	0.0 0.00000	2
HEXACHLOROBENZENE	0.0 0.00000	0.0 0.00000	0.0 0.00000	1.8 23.40000	0.0 0.00000	2
ZINEB	0.4 25.90000	162.7 100.00000	0.0 0.00000	1.2 15.30000	0.0 0.00000	2
STATE TOTALS	1.5	162.7	0.0	7.8	0.0	

STATE EMISSIONS REPORT FOR NORTH CAROLINA

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T

STATE EMISSIONS REPORT FOR NORTH DAKOTA

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T

(continued)

TABLE 28 (continued)

STATE EMISSIONS REPORT FOR OHIO

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T
CAPTAN	0.4 7.28000	0.0 0.00000	0.0 0.00000	6.0 54.60000	0.0 0.00000	2
FOLPET	0.1 1.64000	0.0 0.00000	0.0 0.00000	1.4 12.30000	0.0 0.00000	2
HEXACHLOROBENZENE	0.0 0.00000	0.0 0.00000	0.0 0.00000	1.8 16.40000	0.0 0.00000	2
PENTACHLOROPHENOL AND SODIUM SALTS	5.0 91.10000	0.0 0.00000	0.0 0.00000	1.8 16.40000	0.0 0.00000	2
STATE TOTALS	5.5	0.0	0.0	11.0	0.0	

STATE EMISSIONS REPORT FOR OKLAHOMA

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T

STATE EMISSIONS REPORT FOR OREGON

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T
2,4-D ACID, ESTERS, SALTS	4.5 100.00000	0.0 0.00000	0.0 0.00000	4.5 100.00000	0.0 0.00000	2
STATE TOTALS	4.5	0.0	0.0	4.5	0.0	

(continued)

TABLE 28 (continued)
STATE EMISSIONS REPORT FOR PENNSYLVANIA

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T
2,4-D ACID, ESTERS, SALTS	2.3 50.40000	0.0 0.00000	0.0 0.00000	2.3 24.40000	0.0 0.00000	2
DICOFOL	0.9 20.20000	0.0 0.00000	0.0 0.00000	1.8 19.50000	0.0 0.00000	2
MANEB	0.9 20.20000	372.0 69.60000	0.0 0.00000	2.7 29.20000	0.0 0.00000	2
PROPANIL	0.0 0.00000	0.0 0.00000	0.0 0.00000	1.1 12.20000	0.0 0.00000	2
TEPP	0.0 0.40300	0.0 0.00000	0.0 0.00000	0.2 1.95000	0.0 0.00000	2
ZINEB	0.4 8.83000	162.7 30.40000	0.0 0.00000	1.2 12.80000	0.0 0.00000	2
STATE TOTALS	4.5	534.7	0.0	9.3	0.0	

STATE EMISSIONS REPORT FOR RHODE ISLAND

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T

STATE EMISSIONS REPORT FOR SOUTH CAROLINA

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T

(continued)

TABLE 28 (continued)

STATE EMISSIONS REPORT FOR SOUTH DAKOTA

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T

STATE EMISSIONS REPORT FOR TENNESSEE

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T
DICAMBA	0.0 0.00000	0.0 0.00000	0.0 0.00000	0.9 9.07000	0.0 0.00000	2
ENDRIN	0.0 0.00000	0.0 0.00000	0.0 0.00000	1.4 13.60000	0.0 0.00000	2
HEPTACHLOR	0.0 0.00000	0.0 0.00000	0.0 0.00000	1.4 13.60000	0.0 0.00000	2
MERPHOS	0.0 0.00000	464.9 15.20000	0.0 0.00000	0.0 0.00000	0.0 0.00000	2
METHYL PARATHION	4.5 71.40000	1860.0 60.60000	0.0 0.00000	4.5 45.30000	0.0 0.00000	2
PARATHION	1.8 28.60000	743.9 24.20000	0.0 0.00000	1.8 18.40000	0.0 0.00000	2
STATE TOTALS	6.3	3069.0	0.0	10.0	0.0	

(continued)

TABLE 28 (continued)
STATE EMISSIONS REPORT FOR TEXAS

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T
BROMACIL	0.0 0.00000	0.0 0.00000	0.0 0.00000	2.7 10.30000	0.0 0.00000	2
DICAMBA	0.0 0.00000	0.0 0.00000	0.0 0.00000	1.8 6.85000	0.0 0.00000	2
DICHLOROPROPENE	0.0 0.00000	0.0 0.00000	0.0 0.00000	7.7 29.10000	0.0 0.00000	2
DIURON	0.0 0.00000	0.0 0.00000	0.0 0.00000	2.3 8.56000	0.0 0.00000	2
DSMA	0.0 0.00000	0.0 0.00000	0.0 0.00000	1.3 4.92000	0.0 0.00000	2
LINURON	0.0 0.00000	0.0 0.00000	0.0 0.00000	0.7 2.57000	0.0 0.00000	2
MANEB	0.9 33.30000	372.0 33.30000	0.0 0.00000	2.7 10.30000	0.0 0.00000	2
METHYL PARATHION	0.9 33.30000	372.0 33.30000	0.0 0.00000	0.9 3.42000	0.0 0.00000	2
MONURON	0.0 0.00000	0.0 0.00000	0.0 0.00000	0.2 0.68500	0.0 0.00000	2
MSMA	0.0 0.00000	0.0 0.00000	0.0 0.00000	4.6 17.30000	0.0 0.00000	2
PARATHION	0.9 33.30000	372.0 33.30000	0.0 0.00000	0.9 3.47000	0.0 0.00000	2
TERBACIL	0.0 0.00000	0.0 0.00000	0.0 0.00000	0.7 2.57000	0.0 0.00000	2
STATE TOTALS	2.7	1116.0	0.0	26.5	0.0	

STATE EMISSIONS REPORT FOR UTAH

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T

(continued)

TABLE 28 (continued)

STATE EMISSIONS REPORT FOR VERMONT

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T

STATE EMISSIONS REPORT FOR VIRGINIA

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T

STATE EMISSIONS REPORT FOR WASHINGTON

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF STATE EMISSIONS

SOURCE	PART	SO2	NOX	HC	CO	T
CARBOFURAN	1.1 8.33000	0.0 0.00000	0.0 0.00000	3.4 42.90000	0.0 0.00000	2
PENTACHLOROPHENOL AND SODIUM SALTS	12.5 91.70000	0.0 0.00000	0.0 0.00000	4.5 57.10000	0.0 0.00000	2
STATE TOTALS	13.6	0.0	0.0	7.9	0.0	

(continued)

TABLE 28 (continued)
STATE EMISSIONS REPORT FOR WEST VIRGINIA

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                                         MASS OF EMISSIONS (1000 KG/YR)
                                         PERCENT OF STATE EMISSIONS
     SOURCE
     ------                       PART        SO2         NOX         HC          CO      T
                                  ----        ---         ---         --          --      -
ALDICARB
                                   1.1       464.9         0.0         3.4         0.0    2
                               7.18000    60.20000     0.00000     7.42000     0.00000
CARBARYL
                                  13.1         0.0         0.0        39.5         0.0    2
                              83.30000     0.00000     0.00000    86.00000     0.00000
CDEC
                                   0.2        74.4         0.0         0.5         0.0    2
                               1.15000     9.64000     0.00000     1.19000     0.00000
MLTHOXYCHLOR
                                   0.8         0.0         0.0         0.8         0.0    2
                               4.79000     0.00000     0.00000     1.65000     0.00000
NABAM
                                   0.6       232.5         0.0         1.7         0.0    2
                               3.59000    30.10000     0.00000     3.71000     0.00000

STATE TOTALS
                                  15.8       771.8         0.0        45.9         0.0
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STATE EMISSIONS REPORT FOR WISCONSIN

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                                         MASS OF EMISSIONS (1000 KG/YR)
                                         PERCENT OF STATE EMISSIONS
     SOURCE
     ------                       PART        SO2         NOX         HC          CO      T
                                  ----        ---         ---         --          --      -
CACODYLIC ACID
                                   0.0         0.0         0.0         0.8         0.0    2
                              11.70000     0.00000     0.00000    11.70000     0.00000
DSMA
                                   0.0         0.0         0.0         1.3         0.0    2
                              19.50000     0.00000     0.00000    19.50000     0.00000
MDMA
                                   0.0         0.0         0.0         4.6         0.0    2
                              68.80000     0.00000     0.00000    68.80000     0.00000

STATE TOTALS
                                   0.0         0.0         0.0         6.7         0.0
```

STATE EMISSIONS REPORT FOR WYOMING

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                                         MASS OF EMISSIONS (1000 KG/YR)
                                         PERCENT OF STATE EMISSIONS
     SOURCE
     ------                       PART        SO2         NOX         HC          CO      T
                                  ----        ---         ---         --          --      -
```

TABLE 29. NATIONAL LISTING OF CRITERIA EMISSIONS FROM PRIORITIZED PESTICIDE CHEMICAL MANUFACTURING SOURCES

SOURCE	MASS OF EMISSIONS (1000 KG/YR) PERCENT OF TOTAL INCLUDING METALLURGICAL PROCESSING					
	PART	SO2	NOX	HC	CO	C
ALACHLOR	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.3 0.05180 0.00000	0.0 0.00000 0.00000	2
ALDICARB	1.1 0.53600 0.00000	464.9 2.13000 0.00072	0.0 0.00000 0.00000	3.4 0.64800 0.00002	0.0 0.00000 0.00000	2
ATRAZINE	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	74.8 14.30000 0.00041	0.0 0.00000 0.00000	2
AZINOPHOS - ETHYL	0.7 0.32200 0.00000	0.2 0.00100 0.00000	0.2 1.01000 0.00000	1.0 0.19400 0.00001	0.0 0.00000 0.00000	2
AZINOPHOS - METHYL	0.9 0.42900 0.00000	0.3 0.00133 0.00000	0.2 1.34000 0.00000	1.4 0.25900 0.00001	0.0 0.00000 0.00000	2
BACILLUS THURINGIENSIS	0.5 0.21400 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	2
BENEFIN	1.3 0.61800 0.00000	1.7 0.00797 0.00000	1.3 7.17000 0.00001	0.0 0.00000 0.00000	0.0 0.00000 0.00000	2
BROMACIL	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	2.7 0.51800 0.00001	0.0 0.00000 0.00000	2
BUTACHLOR	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	6.8 1.30000 0.00004	0.0 0.00000 0.00000	2
BUTYLATE	1.8 0.85800 0.00000	743.9 3.40000 0.00115	0.0 0.00000 0.00000	5.4 1.04000 0.00003	0.0 0.00000 0.00000	2
CACODYLIC ACID	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	1.6 0.29800 0.00001	0.0 0.00000 0.00000	2
CALCIUM ACID METHANEARSONATE	--	--	--	--	--	2

(continued)

TABLE 29 (continued)

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF TOTAL INCLUDING METALLURGICAL PROCESSING

SOURCE	PART	SO2	NOX	HC	CO	C
CALCIUM ARSENATE	--	--	--	--	--	2
CAPTAFOL	0.1 0.04250 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	1.4 0.25900 0.00001	0.0 0.00000 0.00000	2
CAPTAN	0.6 0.28300 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	9.1 1.73000 0.00005	0.0 0.00000 0.00000	2
CARBARYL	13.1 6.22000 0.00001	0.0 0.00000 0.00000	0.0 0.00000 0.00000	39.5 7.52000 0.00022	0.0 0.00000 0.00000	2
CARBOFURAN	2.3 1.07000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	6.8 1.30000 0.00004	0.0 0.00000 0.00000	2
CDEC	0.2 0.08580 0.00000	74.4 0.34000 0.00011	0.0 0.00000 0.00000	0.5 0.10400 0.00000	0.0 0.00000 0.00000	2
CHLORAMBEN	--	--	--	--	--	2
CHLORDANE	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	6.8 1.30000 0.00004	0.0 0.00000 0.00000	2
CHLORPYRIFOS	1.1 0.53600 0.00000	464.9 2.13000 0.00072	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	2
2,4-D ACID, ESTERS, SALTS	24.9 11.80000 0.00002	0.0 0.00000 0.00000	0.0 0.00000 0.00000	24.9 4.75000 0.00014	0.0 0.00000 0.00000	2
DALAPON	1.1 0.53600 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	1.1 0.21600 0.00001	0.0 0.00000 0.00000	2
DBCP	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	9.1 1.73000 0.00005	0.0 0.00000 0.00000	2
DDT	13.6 6.43000 0.00001	0.0 0.00000 0.00000	0.0 0.00000 0.00000	27.2 5.18000 0.00015	0.0 0.00000 0.00000	2

(continued)

TABLE 29 (continued)

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF TOTAL INCLUDING METALLURGICAL PROCESSING

SOURCE	PART	SO2	NOX	HC	CO	C
DIAZINON	2.7	1116.0	0.0	0.0	0.0	2
	1.29000	5.11000	0.00000	0.00000	0.00000	
	0.00000	0.00172	0.00000	0.00000	0.00000	
DICAMBA	0.0	0.0	0.0	2.7	0.0	2
	0.00000	0.00000	0.00000	0.51800	0.00000	
	0.00000	0.00000	0.00000	0.00001	0.00000	
DICHLOROPROPENE	0.0	0.0	0.0	11.3	0.0	2
	0.00000	0.00000	0.00000	2.16000	0.00000	
	0.00000	0.00000	0.00000	0.00006	0.00000	
DICHLOROVOS	0.2	0.0	0.0	0.4	0.0	2
	0.08580	0.00000	0.00000	0.06910	0.00000	
	0.00000	0.00000	0.00000	0.00000	0.00000	
DICOFOL	0.9	0.0	0.0	1.8	0.0	2
	0.42900	0.00000	0.00000	0.34600	0.00000	
	0.00000	0.00000	0.00000	0.00001	0.00000	
DICROTOPHOS	0.2	0.0	0.0	0.2	0.0	2
	0.08580	0.00000	0.00000	0.03460	0.00000	
	0.00000	0.00000	0.00000	0.00000	0.00000	
DIMETHOATE	0.7	0.4	0.4	2.7	0.0	2
	0.32200	0.00199	2.02000	0.51800	0.00000	
	0.00000	0.00000	0.00000	0.00001	0.00000	
DINOSEB	1.3	1.7	1.3	1.4	0.0	2
	0.61800	0.00797	7.17000	0.25900	0.00000	
	0.00000	0.00000	0.00001	0.00001	0.00000	
DISULFOTON	2.3	929.9	0.0	0.0	0.0	2
	1.07000	4.25000	0.00000	0.00000	0.00000	
	0.00000	0.00144	0.00000	0.00000	0.00000	
DIURON	0.0	0.0	0.0	2.3	0.0	2
	0.00000	0.00000	0.00000	0.43200	0.00000	
	0.00000	0.00000	0.00000	0.00001	0.00000	
DSMA	0.0	0.0	0.0	5.2	0.0	2
	0.00000	0.00000	0.00000	0.99300	0.00000	
	0.00000	0.00000	0.00000	0.00003	0.00000	
ENDOSULFAN	0.0	0.0	0.0	1.4	0.0	2
	0.00000	0.00000	0.00000	0.25900	0.00000	
	0.00000	0.00000	0.00000	0.00001	0.00000	
ENDRIN	0.0	0.0	0.0	1.4	0.0	2
	0.00000	0.00000	0.00000	0.25900	0.00000	
	0.00000	0.00000	0.00000	0.00001	0.00000	

(continued)

TABLE 29 (continued)

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF TOTAL INCLUDING METALLURGICAL PROCESSING

SOURCE	PART	SO2	NOX	HC	CO	C
EPTC	1.4 0.64300 0.00000	557.9 2.55000 0.00086	0.0 0.00000 0.00000	4.1 0.77700 0.00002	0.0 0.00000 0.00000	2
FENSULFOTHION	1.4 0.64300 0.00000	557.9 2.55000 0.00086	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	2
FLUOMETURON	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	1.1 0.21600 0.00001	0.0 0.00000 0.00000	2
FOLPET	0.1 0.04250 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	1.4 0.25900 0.00001	0.0 0.00000 0.00000	2
HEPTACHLOR	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	1.4 0.25900 0.00001	0.0 0.00000 0.00000	2
HEXACHLOROBENZENE	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	5.4 1.04000 0.00003	0.0 0.00000 0.00000	2
LEAD ARSENATE	--	--	--	--	--	2
LINDANE	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.5 0.08640 0.00000	0.0 0.00000 0.00000	2
LINURON	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.7 0.13000 0.00000	0.0 0.00000 0.00000	2
MALATHION	6.8 3.22000 0.00000	4.4 0.01990 0.00001	3.7 20.20000 0.00002	27.2 5.18000 0.00015	0.0 0.00000 0.00000	2
MANEB	2.7 1.29000 0.00000	1116.0 5.11000 0.00172	0.0 0.00000 0.00000	8.2 1.55000 0.00004	0.0 0.00000 0.00000	2
MERPHOS	0.0 0.00000 0.00000	464.9 2.13000 0.00072	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	2
METALKAMATE (BUX)	2.3 1.07000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	6.8 1.30000 0.00004	0.0 0.00000 0.00000	2

(continued)

TABLE 29 (continued)

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF TOTAL INCLUDING METALLURGICAL PROCESSING

SOURCE	PART	SO2	NOX	HC	CO	C
METHANE ARSENIC ACID	--	--	--	--	--	2
METHOXYCHLOR	2.3 1.07000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	2.3 0.43200 0.00001	0.0 0.00000 0.00000	2
METHYL BROMIDE	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	7.0 1.34000 0.00004	0.0 0.00000 0.00000	2
METHYL PARATHION	23.6 11.20000 0.00002	9671.0 44.20000 0.01490	0.0 0.00000 0.00000	23.6 4.49000 0.00013	0.0 0.00000 0.00000	2
MEVINPHOS	0.2 0.10700 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.2 0.04320 0.00000	0.0 0.00000 0.00000	2
MONOCROTOPHOS	1.6 0.75100 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	1.6 0.30200 0.00001	0.0 0.00000 0.00000	2
MONURON	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.2 0.03460 0.00000	0.0 0.00000 0.00000	2
MSMA	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	18.1 3.46000 0.00010	0.0 0.00000 0.00000	2
NABAM	1.1 0.53600 0.00000	464.9 2.13000 0.00072	0.0 0.00000 0.00000	3.4 0.64800 0.00002	0.0 0.00000 0.00000	2
NALED	0.5 0.21400 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.5 0.08640 0.00000	0.0 0.00000 0.00000	2
PARATHION	7.7 3.65000 0.00001	3162.0 14.50000 0.00488	0.0 0.00000 0.00000	7.8 1.49000 0.00004	0.0 0.00000 0.00000	2
PENTACHLOROPHENOL AND SODIUM SALTS	64.9 30.70000 0.00005	0.0 0.00000 0.00000	0.0 0.00000 0.00000	23.6 4.49000 0.00013	0.0 0.00000 0.00000	2
PHORATE	2.3 1.07000 0.00000	929.9 4.25000 0.00144	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	2

(continued)

TABLE 29 (continued)

MASS OF EMISSIONS (1000 KG/YR)
PERCENT OF TOTAL INCLUDING METALLURGICAL PROCESSING

SOURCE	PART	SO2	NOX	HC	CO	C
PHOSPHAMIDION	0.2 0.08580 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.2 0.03460 0.00000	0.0 0.00000 0.00000	2
PROPACHLOR	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	10.2 1.94000 0.00006	0.0 0.00000 0.00000	2
PROPANIL	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	3.4 0.64800 0.00002	0.0 0.00000 0.00000	2
PROPAZINE	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	6.8 1.30000 0.00004	0.0 0.00000 0.00000	2
PYRETHINS	0.5 0.25700 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.5 0.10400 0.00000	0.0 0.00000 0.00000	2
RONNEL	0.5 0.21400 0.00000	0.3 0.00133 0.00000	0.2 1.34000 0.00000	1.8 0.34600 0.00001	0.0 0.00000 0.00000	2
SILVEX	0.7 0.32200 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	1.4 0.25900 0.00001	0.0 0.00000 0.00000	2
SIMAZINE	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	10.2 1.94000 0.00006	0.0 0.00000 0.00000	2
SODIUM TCA	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	6.8 1.30000 0.00004	0.0 0.00000 0.00000	2
TEPP	0.0 0.00858 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.2 0.03460 0.00000	0.0 0.00000 0.00000	2
TERBACIL	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	0.7 0.13000 0.00000	0.0 0.00000 0.00000	2
TOXAPHENE	0.0 0.00012 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	63.9 12.20000 0.00035	0.0 0.00000 0.00000	2
TRICHLOROPHENOLS	5.7 2.68000 0.00000	0.0 0.00000 0.00000	0.0 0.00000 0.00000	11.3 2.16000 0.00006	0.0 0.00000 0.00000	2

(continued)

TABLE 29 (continued)

SOURCE	PART	SO2	NOX	HC	CO	C
	MASS OF EMISSIONS (1000 KG/YR) PERCENT OF TOTAL INCLUDING METALLURGICAL PROCESSING					
TRIFLURALIN	10.9 5.15000 0.00001	14.5 0.06640 0.00002	10.9 59.80000 0.00005	0.0 0.00000 0.00000	0.0 0.00000 0.00000	2
VERNOLATE	1.1 0.53600 0.00000	464.9 2.13000 0.00072	0.0 0.00000 0.00000	3.4 0.64800 0.00002	0.0 0.00000 0.00000	2
ZINEB	1.6 0.75100 0.00000	650.9 2.98000 0.00101	0.0 0.00000 0.00000	4.8 0.90700 0.00003	0.0 0.00000 0.00000	2
TOTALS FOR PESTICIDES	211.5	21860.0	18.2	525.1	0.0	
TOTALS FOR ALL U. S. SOURCES	136200000.0	64740000.0	22360000.0	18150000.0	97340000.0	

SECTION 7

GROWTH AND NATURE OF THE INDUSTRY

GOVERNMENT REGULATION

EPA has assumed federal authority over pesticide regulations, taking over previous responsibilities belonging to the Departments of Agriculture (USDA); Interior; and Health, Education, and Welfare. The Office of Pesticide Programs of the EPA has canceled or suspended some or all uses of certain pesticides, including many of the chlorinated hydrocarbon insecticides and mercury-containing fungicides.

Pesticides are presently controlled under the Federal Insecticide, Fungicide, and Rodenticide Act of 1947 (FIFRA) as amended by the Federal Environmental Pesticide Control Act of 1972 (FEPCA). FEPCA expanded provisions of the 1947 Act, giving EPA new authority to classify chemicals for restricted use (only licensed applicators may apply the pesticide), to regulate the use of products in addition to specifying labeling, and to control products sold in interstate commerce.

In December 1972, acting as the enforcement agency for the Federal Insecticide, Fungicide and Rodenticide Act of 1947 as amended in 1972, EPA placed a near-total ban on domestic use of DDT (11). The ban resulted partly from the exceptional persistence of DDT. Because it degrades very slowly and is stored in the fat of living organisms, it tends to build up in the natural food chain and accumulate in the tissues of fish, wildlife, and humans. Deciding that the compound is a cancer hazard in humans, the agency ordered it almost completely off the market. Use of DDT had already declined greatly, however, due to its ineffectiveness against increasingly resistant insects.

The near-total banning of DDT in the United States has not had major adverse effects on American agriculture. In its largest uses, on cotton and soybeans, it has been replaced by methyl parathion. This organophosphorus insecticide is less persistent than DDT, but it is much more toxic to humans and generally must be used more often for proper insect control. Another chemical used as a replacement for DDT to control insects on cotton and soybeans is toxaphene. This organochlorine insecticide is often used in combination with methyl parathion to increase its effectiveness against specific insects and to expand the range of insects against which the formulation is active (11).

For controlling insects on fruit, DDT has been replaced by such compounds as parathion, malathion, guthion, carbaryl, and phosmet. For control of insects on vegetables and in home and garden applications, DDT has been replaced by such compounds as malathion, carbaryl, phosmet, methoxychlor, diazinon, and oxydemeton-methyl. In controlling forest insects, the leading substitutes for DDT include carbaryl, trichlorfon, and fenitrothion. For mosquito control, the chief DDT replacements include malathion, parathion, methyl parathion, fenthion and dursban (11). A total of 24 pesticides have been identified as potential DDT substitutes.

In October 1974, EPA called a halt to formulation and sale of two organochlorine insecticides, aldrin and dieldrin, for all but a few uses (11). EPA action was based on findings that laboratory rats and mice fed dieldrin (a metabolite of aldrin) developed cancerous liver tumors. Dieldrin has also been found in foods, such as dairy products, and in human fatty tissue; thus EPA concluded that aldrin and dieldrin were a cancer threat to humans.

Among available replacements for aldrin and dieldrin in controlling insects on corn and other crops are carbaryl, diazinon, carbofuran, phorate, fensulfothion, fonofos, and chlorpyrifos. All of these compounds are less persistent than aldrin and dieldrin (11).

In November 1974, EPA similarly issued a notice of intent to cancel its registration of two other related organochlorine insecticides, chlordane and heptachlor, because heptachlor epoxide (a metabolite of both insecticides) has been found to cause cancerous tumors in laboratory rats and mice. Residues of heptachlor epoxide have been found in food, human fatty tissue, and human milk (11).

Among the available alternatives to chlordane and heptachlor in treating corn and other crops are carbofuran, phorate, carbaryl, diazinon, parathion, methomyl, and disulfoton. These alternatives are not as long-lived in most instances and must be applied more often (11).

Several uses for the herbicide 2,4,5-T and the fungicides ethylene dis(dithiocarbamates) (EBDC) have also been restricted. Similarly, kepone-containing compounds were banned due to their carcinogenicity. Mirex, which degrades to kepone, was recently dropped by Allied Chemical and production was left to the State of Mississippi (5).

EPA has recently initiated a program in cooperation with the industry to develop more acceptable substitute pesticides. The 29 substitute insecticides shown in Table 30 have been identified as potential replacements for the five restricted chlorinated hydrocarbon insecticides shown. In addition, eight herbicides (bromacil, MSMA/DSMA, cacodylic acid, dinoseb, dicamba, monuron, simazine, and trifluralin) were nominated to replace 2,4,5-T, but cacodylic acid is currently under a rebuttal presumption against registration, and monuron has been shown to have carcinogenic properties. Three fungicides (captan, PCNB, and folpet) are potential substitutes for EBDC (5).

TABLE 30. PROPOSED SUBSTITUTE INSECTICIDES (5)
(Registrations cancelled)

Proposed substitutes	DDT	Aldrin	Dieldrin	Chlordane	Heptachlor
Phorate	X	X		X	X
Demeton	X				
Methyl parathion	X				
Parathion	X	X		X	X
Malathion	X				
Guthion	X				
Aldicarb	X				
Azodrin	X				
Diazinon	X	X		X	X
Dimethoate	X				
Fenthion	X				
Methomyl	X				
Crotoxyphos	X				
Chlorpyrifos	X	X		X	X
Buxten		X		X	X
Carbonfuran	X	X		X	X
Counter		X		X	X
Dasanite	X	X		X	X
Disulfoton	X	X		X	X
Dyfonate	X	X		X	X
Landrin		X		X	X
Trichlorfon	X	X		X	X
Dacthal				X	
Aspon	X	X	X	X	
Siduron				X	
Ethion	X	X	X	X	
Propoxur	X	X	X	X	X
Acephate	X		X	X	
Methoxychlor	X		X	X	

It appears that the EPA will attempt to evaluate both the benefits and the environmental hazards and other risks connected with pesticide use before granting new registrations or issuing suspensions or cancellations. For each pesticide under review, the EPA will examine data regarding the degree of control achieved and the probable damage that would occur without the use of the chemical, and will also determine whether safe and effective substitutes are available. Rather than ordering a widespread cancellation of pesticide use, it appears likely that the agency will order reductions in applications of persistent and hazardous agents without sacrificing essential uses. The degree of enforcement will largely depend on the availability of economically feasible alternatives to the chemicals; however, indiscriminate use of persistent or toxic chemicals will not be allowed. The EPA will be pressuring the pesticide industry to develop alternate methods of pest control (20).

ALTERNATIVES TO PESTICIDE CHEMICALS

Due to increasingly stringent regulations, rising costs, and insect resistance to pesticide chemicals, changes are occurring in pest control strategies. Emphasis is being placed on effective or adequate control of pests with minimum environmental contamination (20).

There have been a variety of new approaches to pest control during the last several years. The concept of integrated pest management dates back to the 1950's and has come to mean the optimum application of all techniques to realize economical control with minimum ill effects on nontarget species, the food chain, and the environment. Integrated pest management techniques, many of which may grow in importance, are listed in Table 31 (5).

Behavioral manipulation refers to a technique designed to affect the communication systems of pests by sending special signals or altering existing signals. Insects are very sensitive to odors, and very small quantities of insect attractants can be used to lure them to traps (21). The attractants, which are usually food- or sex-based, may be effective for distances up to 1.6 km. They are usually highly specific, attracting only a few closely related species, and then often only males. Attractants may be used either to monitor the presence of a pest or in bait traps, to which large numbers of males would be drawn and destroyed.

Another promising technique of pest management is the use of juvenile hormones. Also called insect growth regulators, these compounds do not kill, but instead interfere with the insect's normal development. Altosid SR-10, a juvenile hormone recently approved by the EPA for commercial use, is imbedded in a slow-release matrix of 1-μm-diameter polymer spheres. The water suspension has shown low toxicity to nontarget species; it degrades rapidly, and small volumes are required (5).

Genetic manipulation is another technique of integrated pest control that is receiving increased attention. It takes two

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(20) Connolly, E. M. Pesticides. Stanford Research Institute, Menlo Park, California, 1973. 24 pp.

(21) Edwards, C. A. Persistent Pesticides in the Environment. CRC Press, Cleveland, Ohio, 1970. 78 pp.

TABLE 31. INTEGRATED PEST MANAGEMENT OPTIONS (5)

Traditional chemical manipulation	Herbicides	
	Insecticides	
	Fungicides	
Behavioral manipulations	Juvenile hormones	
	Pheromones	
Environmental manipulations	Plant spacing	
	Crop rotation	
	Water management	
	Soil preparation (plowing cultivation, destruction of crop residues)	
	Sanitation	
	Fertilization	
	Mixed plant culture	
	Planting time	
	Land use management	
	Regional crop planting	
	Timing of flooding	
	Vegetation clearings	
	Metal guards	
	Isolation, quarantine	
Genetic manipulations	Resistant varieties (genetics resistance)	
	Lethal genes	
	Male producing genes	
	Generation control genes	
	Cytoplasmic incompatibility	
	Chromosone translocations	
	Gene replacement	
	Sterile male	
Ecology manipulations	Natural Enemies	Parasite
		Predator
		Pathogen
	Competition	
	Eradication of alternate hosts	

basic forms: development of crop varieties genetically resistant to pests, and use of genetically modified members of pest species (such as sterile males) to interfere with reproduction or other functions. Chromosome modification, usually leading to pests that produce no offspring or offspring with lethal genes, is under intensive study. Genetic techniques will probably be used only on specialized groups, in limited areas, and for special problems. Massive use of these techniques is not close at hand (5).

Living insecticides (bacteria, viruses, fungi, protozoa, and parasitic nematodes) are also receiving a great deal of attention as a method of pest control. *Bacillus thuringiensis* (BA-068), a strain of spore-forming bacterium, has been mass produced and tested to suppress a variety of aquatic mosquitoes. Currently, research and development of viral pesticides (polyhedrosis viruses) is being conducted, and field tests indicate that their degree of control is as good as that of chemical pesticides. A great deal of work remains in developing suitable formulations for large-scale manufacturing and application.

Opportunities for new pesticide chemicals will, of course, continue. The average life expectancy of a pesticide is estimated to be about 10 yr, during which time cheaper, more effective and safer compounds are developed. Several organic pesticides, however, are exhibiting life-spans far in excess of 10 yr.

Typical examples are: zineb (1943); dinoseb (1945); methyl parathion (1947); captan and parathion (1949); maneb and malathion (1950); diazinon (1952); dalapon and guthion (1953); phorate, diuron, and EPTC (1955); disulfoton, carbaryl, and simazine (1956); atrazine, chloramben, and paraquat (1958); and fenitrothion (1959) (5).

Many new pesticide chemicals are entering the market. Among the promising ones are (5):

- Ansar 529 H.C. Ansul was granted an experimental permit in 1975 to test this herbicide aimed at wild oat, green foxtail, and mustard weeds in oats.

- Sevin 4 oil carbaryl. Union Carbide obtained registration in 1976 for this insecticide which protects spruce and fir foliage against the spruce budworm.

- Galecron. Ciba-Geigy began production of this chemical (also called chlordimeform) in 1976. It is used against the budworm, bollworm, and leaf perforator, with insecticide use on a number of fruits indicated.

- Terbufos. Developed early in 1975 by American Cyanamid, this chemical controls corn rootworm, and EPA approval is expected for use on seed corn and popcorn.

- Dialifor. Also called Torak®, this product was introduced in 1973 by Hercules for mite control in citrus orchards. Registration has since been extended to nut tree insects, grape leafhoppers, and apple coddling moths.

- NRDC-143 (permethrin). The chemical is a new pyrethroid tested by FMC that is stable in sunlight for more than 4 days. Success with this product could trigger widespread interest in pyrethroids.

- FMC-25213. The new dioxane preemergence herbicide introduced by FMC controls nutsedge, Johnson grass, and Bermuda grass.

- Destun®. This product, with a common name of perfluidone diethanol amine, signals the entry of 3M into the farm chemicals business. Destun® is used to control nutsedge.

- Elcar. This natural virus insecticide attacks bollworms and tobacco budworms.

- Glyphosphate. This herbicide, developed by Monsanto and marketed under the "Roundup®," has received considerable interest due to its efficacy and unique mode of action as an inhibitor of the biosynthesis of aromatic amino-acids (22). Roundup® offers effective postemergent control of many emerged annual and perennial broadleaves and grasses.

Environmental, economic, and social pressures have led to laboratory studies such as synergism, low-volume and ultra-low-volume application rates, and controlled-release systems such as pesticide microencapsulation, promising cheaper and safer products in the future.

FUTURE PRODUCTION

Chemical pesticides should continue to be significant in pest management despite changes in pest control strategies. The primary reason for their continuing use is the inability of other methods to maintain adequate control. Overall, however, future developments in chemical pest control may decelerate due to restrictive conditions dampening the expansion programs of manufacturers.

Pesticide production beyond the next few years is difficult to estimate because of diverse changes in government regulation, the influence of research on new products and on application rates of products, and a variety of economic factors. The U.S. pesticide market will largely depend on world agriculture and population. Presently, agriculture takes 59% of domestic pesticide production to keep pest population below the level at which crop damage costs exceed control costs (5).

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(22) Bronstad, J. O., and H. O. Friestad. Method for Determination of Glyphosphate Residues in Natural Waters Based on Polarography of the *N*-Nitroso Derivative. Analyst, 101: 820-824, October 1976.

Future agricultural markets are likely to consist of fewer but larger farms, technically and commercially more sophisticated farmers, and increasing specialization in application of knowledge. Integration of farm, industrial, and technical-service labor is likely. There will be shifts in types of major crops and growing areas, and controlled environments for food production may become a factor (20).

The growth of chemical pesticides in the United States is not likely to continue the fast pace of the 1960's for several reasons. Growth in the use of herbicides, which are primarily responsible for the expansion of the pesticide market in recent years, should be slowing. In addition, many pesticide applications are nearing the practical saturation level. Moreover, concern about environmental pollution and hazards, resulting in stricter regulations and higher costs, should lead to less use of chemicals as well as more efficient application techniques. These influences will limit the growth in production of pesticides, primarily insecticides.

Factors that would tend to expand the pesticide market include: less persistent pesticides will have to be applied more often; in case of a drought or increased food demand, additional crop acreage may be needed; rapid infestation in any 1 yr will increase pesticide need; and some applications have not yet reached a saturation level (20).

Figure 29 shows the estimated growth of synthetic organic pesticides to 1985 based on an annual average growth rate of 1% for the total (20). Insecticide production in 1985 should remain at approximately the current level. Herbicide use will not resume the dramatic increases of the 1960's but should rise about 2% annually to 1985. The fungicide market should grow at a comparatively slow rate, approximately 1.8% annually, for the following reasons. Annual fungicide consumption varies much more than that of other types of pesticides because of the greater variations in pathogenic activity, making producers less inclined to undertake costly R&D to meet complex registration requirements. In addition, several relatively inexpensive, established products are still effective, and current markets are fairly well saturated (20).

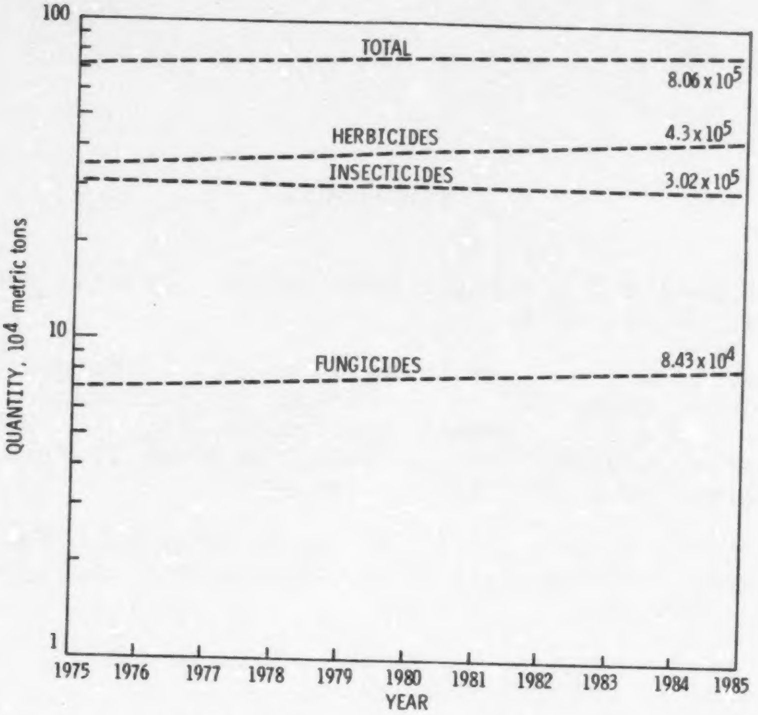

Figure 29. U.S. estimated average annual growth of synthetic organic pesticides (20).

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APPENDIX A

PREDICTION OF PESTICIDE AND AMMONIA EMISSIONS FROM HOLDING PONDS AND EVAPORATION LAGOONS

INTRODUCTION

Following chemical treatment, liquid wastes from pesticide manufacturing often go to a holding pond or evaporation lagoon where evaporation of undestroyed hazardous material can occur, resulting in emission to the atmosphere. Data reqarding pesticide emissions from ponds and lagoons are virtually nonexistent; equations were therefore utilized to develop emission factors for these sources for use in the prioritization of pesticide chemical source types. This appendix presents background information, equations, and calculations used to develop emission factors for both pesticides and ammonia from holding ponds and evaporation lagoons. The next section of this appendix deals with pesticide emissions, and the following section deals with ammonia desorption.

PESTICIDE EMISSIONS FROM HOLDING PONDS AND LAGOONS

Background

Evaporation of a pesticide from the surface of a holding pond or evaporation lagoon depends upon the vapor pressure of the compound, its solubility in water, and the amount of pesticide truly in solution. The characteristic low solubility of pesticides in water yields only very dilute ideal solutions for which Henry's Law is obeyed. Henry's Law specifies that the vapor pressure over the solution is proportional to both the vapor pressure of the pure compound and the relative saturation of the solution (23). Evaporation rates of pesticides from water, however, can be very high (24).

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(23) Glotfelty, D. E., and J. H. Caro. Introduction, Transport, and Fate of Persistent Pesticides in the Atmosphers. In: Removal of Trace Contaminants from the Air, V. R. Deitz, ed. American Chemical Society, Washington, D.C., 1975. 207 pp.

(24) Mackay, D., and A. W. Wolkoff. Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to Atmsophere. Environmental Science and Technology, 7(9):611-614, 1973.

Pesticides are generally of high molecular weight and low vapor pressure, so it would appear that the evaporation rate would be slow. A factor that is often overlooked is the remarkably high activity coefficients of these compounds in water, which cause unexpectedly high equilibrium vapor partial pressures and, thus, high evaporation rates (24).

Equations

The approach taken in Reference 24 to predict evaporation rates from natural waters is to calculate, from equilibrium thermodynamic considerations, the composition of vapor in equilibrium with the water solution. The following assumptions were made:

- The contaminant concentration is that truly in solution, not in suspended, colloidal, ionic, complexed, or absorbed form.
- The vapor formed is in equilibrium with the liquid at the interface. This is generally accepted as applying to phase change mass transfer processes such as distillation.
- The water mixing or the pesticide diffusion in water is sufficiently fast that the concentration at the interface is close to that of the bulk of the water. The validity of this assumption depends on the relative rates of evaporation and diffusion or mixing. The slower of these two will tend to control the overall rate.
- The water evaporation rate is negligibly affected by the presence of the contaminant. This assumption is valid for low concentrations of nonsurface-active compounds.

The validity of these assumptions can be confirmed only by experimental data, few of which are available. The evaporation equations should represent the physical processes involved with reasonable accuracy for prioritization.

The equations presented in Reference 24 were modified slightly by incorporating a surface area factor in order to provide a total emission rate from the surface of a pond or lagoon. Two cases are considered: first, evaporation occurs from a saturated solution of pesticide "i" containing excess i as a separate phase.

$$C_{io} - C_i = EP_{is}M_i tA10^6/(GM_w P_w) \qquad \text{(A-1)}$$

where C_{io} = initial concentration of pesticide "i", g/m^3

C_i = concentration of "i" at time t, g/m^3

E = water evaporation rate, g/m^2-day

P_{is} = vapor pressure of pure solid or liquid "i", Pa
M_i = molecular weight of "i", g/mole
t = time, days
A = surface area, m^2
10^6 = conversion factor, molar to g/m^3
G = weight of water body, g
M_w = molecular weight of water, g/mole
P_w = vapor pressure of water, Pa

In the second case, evaporation takes place from a solution in which "i" is present at a concentration less than saturation:

$$\ln(C_{io} - C_i) = EP_{is}M_itA10^6/(GM_wP_wC_{is}) \quad \text{(A-2)}$$

where C_{is} = saturation concentration of i, g/m^3

Equation A-2 may be modified to the following form:

$$(C_{io} - C_i) = C_{io}\left\{1 - \frac{1}{\exp[(EP_{is}M_itA10^6)/(GM_wP_wC_{is})]}\right\} \quad \text{(A-3)}$$

In summary, if "i" is present in water at a concentration above its saturation value and the solution remains saturated, the change in concentration due to evaporation will be described by Equation A-1 until its concentration equals the saturation value. The change in concentration will then be described by Equation A-3.

Equations A-1 and A-3 give the change in pesticide concentration due to evaporation from saturated and undersaturated solutions, respectively. The evaporation rate, dm_i/dt is determined by substituting $(C_{io} - C_i)$ into the following equation:

$$\frac{dm_i}{dt} = \left[\frac{(C_{io} - C_i)}{t}\right]V \quad \text{(A-4)}$$

where dm_i/dt = pesticide evaporation rate, g/day (when t = 1 day)
t = time, days (1 day)
V = volume of water body, m^3

Simplifying gives Equation A-5 and Equation A-6, which predict the evaporation rate of pesticide "i" in g/day from a saturated solution and from a solution in which "i" is present at a concentration less than saturation, respectively. Thus, the evaporation rate of pesticide "i" from a saturated solution, in g/day, is predicted as follows:

$$\frac{dm_i}{dt} = \frac{EP_{is}M_iAV10^6}{GM_wP_w} \qquad \text{(A-5)}$$

Similarly, the evaporation rate of pesticide "i", in g/day, from a solution in which "i" is present at a concentration less than saturation is predicted as follows:

$$\frac{dm_i}{dt} = \frac{VC_{io}}{t}\left[1 - \frac{1}{\exp(EP_{is}M_itA10^6/GM_wP_wC_{is})}\right] \qquad \text{(A-6)}$$

Several assumptions were made in order to use Equations A-5 and A-6 in the prioritization. First, the ambient temperature was chosen to be 25°C, yielding a water vapor pressure (P_w) equal to approximately 3.2×10^3 Pa and the physical properties of the five pesticides listed in Table A-1 (24-27). The evaporation rate of water was chosen as 2,740 g/m^2-day, corresponding to a water evaporation rate of approximately 1,000 mm/yr. Time was assumed to be 1 day, giving an emission rate in g/day.

TABLE A-1. PESTICIDE PHYSICAL PROPERTIES AT 25°C

Pesticide	Molecular weight, g/mole	Vapor pressure, Pa	Solubility, g/m^3
Aldrin	364.9 (25)	8.0×10^{-4} (24)	2×10^{-1} (26)
DDT	306.5 (25)	1.3×10^{-5} (24)	3.7×10^{-1} (26)
Dieldrin	381.0 (25)	1.3×10^{-5} (24)	2.5×10^{-1} (26)
Methyl parathion	263.2 (27)	1.3×10^{-3}[a] (27)	60 (27)
Toxaphene	413.8 (25)	1.3×10^{-1}[b]	4×10^{-1} (26)

[a] Vapor pressure at 20°C.

[b] Actual vapor pressure ranges from 27 Pa to 53 Pa at 25°C, but a ceiling value of 1.3×10^{-1} Pa was imposed. The ceiling value was determined by plotting predicted emission rates versus vapor pressure for several vapor pressures. The results showed an exponential increase above a vapor pressure of 1.3×10^{-1}.

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(25) Kenaga, E. E. Pesticide Reference Standards of the Entomological Society of America. Bulletin of the Entomological Society of America, 12:117-127, 1966.

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(27) Substitute Chemical Program: Initial Scientific and Minieconomic Review of Methyl Parathion. EPA-540/1-75-004, U.S. Environmental Protection Agency, Washington, D.C., February 1975. 176 pp.

Calculations

Dieldrin--

Assume evaporation takes place from a 4.05×10^5 m^2 concrete-lined evaporation lagoon, 1 m deep, with a dieldrin concentration equal to 5 g/m^3. The lagoon dimensions give the following parameters:

$$A = 4.05 \times 10^5 \text{ m}^2$$
$$V = 3.70 \times 10^5 \text{ m}^3$$
$$G = 3.70 \times 10^{11} \text{ g}$$

The dieldrin concentration is above saturation, thus Equation A-5 is used as follows:

$$\frac{dm_i}{dt} = \frac{EP_{is}M_iAV10^6}{GM_wP_w} \tag{A-5}$$

where dm_i/dt = evaporation rate of dieldrin, g/day
E = 2,740 g/m^2-day
P_{is} = 1.3×10^{-5} Pa
M_i = 381.0 g/mole
A = 4.05×10^5 m^2
V = 3.70×10^5 m^3
10^6 = conversion factor, g/m^3
G = 3.70×10^{11} g
M_w = 18 g/mole
P_w = 3.2×10^3 Pa

Thus, dm_i/dt = 95.4 g/day = 34.8 kg/yr.

Assuming dieldrin production to be equal to 340 metric tons/yr, the emission factor for dieldrin evaporation is calculated as follows:

$$\frac{34.8 \text{ kg/yr}}{340 \text{ metric tons/yr}} = 1.19 \times 10^{-1} \text{ kg/metric ton}$$

Aldrin--

Assume evaporation takes place from a 4.05×10^5 m^2 concrete-lined evaporation lagoon, 1 m deep, with an aldrin concentration equal to 5 g/m^3. The lagoon dimensions give the following parameters:

$$A = 4.05 \times 10^5 \text{ m}^2$$
$$V = 3.70 \times 10^5 \text{ m}^3$$
$$G = 3.70 \times 10^{11} \text{ g}$$

The aldrin concentration is above saturation, thus Equation A-5 is used as follows:

$$\frac{dm_i}{dt} = \frac{EP_{is}M_iAV10^6}{GM_wP_w} \qquad \text{(A-5)}$$

where dm_i/dt = evaporation rate of aldrin, g/day

E = 2,740 g/m^2-day

P_{is} = 8.0×10^{-4} Pa

M_i = 364.9 g/mole

A = 4.05×10^5 m^2

V = 3.70×10^5 m^3

10^6 = conversion factor, g/m^3

G = 3.70×10^{11} g

M_w = 18 g/mole

P_w = 3.2×10^3 Pa

Thus, $dm_i/dt = 5.6 \times 10^3$ g/day $= 2.05 \times 10^3$ kg/yr.

Annual production of aldrin is estimated as 4.5×10^3 metric tons (2), giving an aldrin emission factor equal to 4.6×10^{-1} kg/metric ton.

DDT--

Assume evaporation takes place from a holding-recycle pond with a surface area equal to 348 m^2, depth equal to 4.6 m, and a DDT concentration of 10 g/m^3 to 15 g/m^3. The pond dimensions give the following parameters:

A = 348 m^2
V = 1,590 m^3
G = 1.59×10^9 g

The DDT concentration is above saturation, thus Equation A-5 is used as follows:

$$\frac{dm_i}{dt} = \frac{EP_{is}M_iAV10^6}{GM_wP_w} \qquad \text{(A-5)}$$

where dm_i/dt = evaporation rate of aldrin, g/day

E = 2,740 g/m^2-day

P_{is} = 1.3×10^{-5} Pa

M_i = 306.5 g/mole

A = 348 m^2

$V = 1{,}590\ \text{m}^3$
10^6 = conversion factor, g/m^3
$G = 1.59 \times 10^9$ g
M_w = 18 g/mole
$P_w = 3.2 \times 10^3$ Pa

Thus, $dm_i/dt = 6.6 \times 10^{-2}$ g/day $= 2.4 \times 10^{-2}$ kg/yr.

Annual DDT production is estimated to be 27.2×10^3 metric tons (2), giving a DDT emission factor equal to 8.8×10^{-7} kg/metric ton.

Toxaphene--
Assume evaporation takes place from two settling ponds (each with dimensions 61 m x 122 m x 1 m deep) at a concentration above saturation. The ponds' dimensions give the following parameters:

$A = 1.49 \times 10^4\ \text{m}^2$
$V = 1.36 \times 10^4\ \text{m}^3$
$G = 1.36 \times 10^{11}$ g

The toxaphene concentration is above saturation, thus Equation A-5 is used as follows:

$$\frac{dm_i}{dt} = \frac{EP_{is}M_iAV10^6}{GM_wP_w} \qquad \text{(A-5)}$$

where dm_i/dt = evaporation rate of toxaphene, g/day
$E = 2{,}740$ g/m^2-day
$P_{is} = 1.3 \times 10^{-1}$ (from Table A-1)
M_i = 413.8 g/mole
$A = 1.49 \times 10^4\ \text{m}^2$
$V = 1.36 \times 10^4\ \text{m}^3$
10^6 = conversion factor, g/m^3
$G = 1.36 \times 10^{10}$ g
M_w = 18 g/mole
$P_w = 3.2 \times 10^3$ Pa

Thus, $dm_i/dt = 3.8 \times 10^4$ g/day $= 1.4 \times 10^4$ kg/yr.

Annual toxaphene production is estimated to be 49.9×10^3 metric tons/yr (2), giving a toxaphene emission factor equal to 2.8×10^{-1} kg/metric ton.

Methyl parathion--
Assume evaporation takes place from a holding pond (22.9 m x 15.2 m x 4.6 m deep) and methyl parathion is in solution at a concentration of 5 g/m^3. The pond geometry gives the following parameters:

$$A = 348\ m^2$$
$$V = 1.6 \times 10^3\ m^3$$
$$G = 1.6 \times 10^9\ g$$

Methyl parathion is in solution at a concentration below its saturation value of 60 g/m^3, thus use Equation A-6 as follows:

$$\frac{dm_i}{dt} = \frac{VC_{io}}{t}\left[1 - \frac{1}{\exp(EP_{is}M_i tA10^6/GM_w P_w C_{is})}\right] \qquad \text{(A-6)}$$

where dm_i/dt = evaporation rate of methyl parathion, g/day

$V = 1.6 \times 10^3\ m^3$

$C_{io} = 5\ g/m^3$

$E = 2{,}740\ g/m^2\text{-day}$

$P_{is} = 1.3 \times 10^{-3}$ Pa

$M_i = 263.2$ g/mole

$t = 1$ day

$A = 348\ m^2$

10^6 = conversion factor, g/m^3

$G = 1.6 \times 10^9$ g

$M_w = 18$ g/mole

$P_w = 3.2 \times 10^3$ Pa

$C_{is} = 60$ g/m

Thus, $dm_i/dt = 4.7 \times 10^{-2}$ g/day $= 1.7 \times 10^{-1}$ kg/yr.

Methyl parathion annual production is estimated to be 23.1×10^3 metric tons (2), and the emission factor for evaporation is calculated as follows:

$$\frac{1.7 \times 10^{-1}\ \text{kg/yr}}{23.1 \times 10^3\ \text{metric tons/yr}} = 7.4 \times 10^{-6}\ \text{kg/metric ton}$$

AMMONIA EMISSIONS FROM HOLDING PONDS AND LAGOONS

Equation

Ammonia emission to the atmosphere can occur from aerated wastewater treatment systems as well as from holding ponds and evaporation lagoons. The following equation has been presented in the literature to predict the change in ammonia concentration due to desorption from a continuous flow system (28):

$$\frac{C_1 - C_2}{C_2} = K_D \cdot F_r \cdot t_{HR} \qquad \text{(A-7)}$$

where C_1 = total ammoniacal nitrogen at time t_1, g/m^3

C_2 = total ammoniacal nitrogen at time t_2, g/m^3

K_D = operational desorption coefficient, hr^{-1}

F_r = ratio of undissociated ammonia to the total ammoniacal nitrogen in solution

t_{HR} = hydraulic retention time, hr

The change in ammonia concentration, determined by Equation A-7, is subsequently multiplied by the volume of water in the treatment unit and the number of hydraulic retention times per day to give the ammonia desorption rate in g/day.

The operational desorption coefficient (K_D) and the ratio of undissociated ammonia to the total ammoniacal nitrogen in solution (F_r) must be calculated for use in Equation A-7.

Determination of K_D--

Determined by direct experimentation or semiempirical relationships, K_D is a system-dependent desorption coefficient and a function of both environmental and process conditions. Equation A-8 is used to calculate K_D for quiescent systems.

$$K_D = 0.021 \exp[0.062(\theta-5)] \qquad \text{(A-8)}$$

where θ = temperature, °C

Determination of F_r--

The ratio of undissociated ammonia nitrogen, which can be removed by desorption, to total ammoniacal nitrogen is represented by F_r. Assuming that total ammoniacal nitrogen may be approximated by total Kjeldahl nitrogen (TKN), the following relationship is developed for F_r:

$$F_r \cong \frac{NH_3N}{TKN} = \frac{\text{undissociated ammonia nitrogen}}{\text{total Kjeldahl nitrogen}}$$

As shown in Figure A-1, F_r varies with temperature and pH (27). Little or no desorption occurs below a pH of about 7.

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(28) Srinath, E. G, and R. C. Loehr. Ammonia Desorption by Diffused Aeration. Journal of the Water Pollution Control Federation, 46(8):1939-1957, 1974.

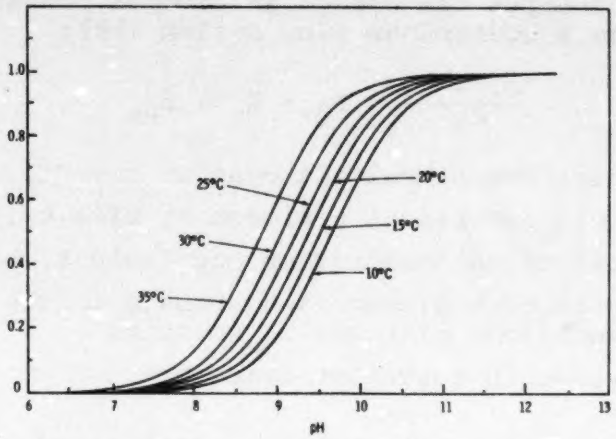

Figure A-1. Effect of pH and temperature on fraction of undissociated ammonia (28).

Values of F_r for specific values of pH and temperature are presented in Table A-2 (28).

TABLE A-2. VALUES OF F_r AT DIFFERENT pH AND TEMPERATURES (28)

Temp.,	pH								
°C	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5	11.0
10	0.002	0.006	0.020	0.061	0.170	0.393	0.672	0.866	0.953
15	0.003	0.009	0.028	0.082	0.221	0.473	0.739	0.900	0.966
20	0.004	0.012	0.037	0.110	0.280	0.552	0.796	0.925	0.975
25	0.005	0.017	0.052	0.148	0.354	0.634	0.846	0.945	0.982
30	0.008	0.025	0.076	0.207	0.452	0.723	0.892	0.963	0.998
35	0.014	0.043	0.125	0.312	0.589	0.819	0.935	0.978	0.993

Calculation

For methyl parathion, assume ammonia desorption occurs from a holding pond (22.9 m x 15.2 m x 4.6 m deep) with a hydraulic retention time equal to 24 hr. Assuming a pH of 10 and a temperature of 25°C, F_r equals 0.846 from Table A-2. From Equation A-8, K_D equals 0.073 hr^{-1} at a temperature of 25°C.

The change in ammonia concentration is calculated by Equation A-7:

$$\frac{C_1 - C_2}{C_2} = K_D \cdot F_r \cdot t_{HR} \qquad \text{(A-7)}$$

Assuming that C_1 (the total ammoniacal nitrogen at time t_1) may be approximated by TKN and assuming TKN for the untreated wastewater is 3.0 g/m^3, Equation A-7 may be solved for C_2.

$$\frac{3.0\ \text{g/m}^3 - C_2}{C_2} = (0.073\ \text{hr}^{-1})(0.846)(24\ \text{hr})$$

$$\therefore C_2 = 1.2\ \text{g/m}^3$$

The change in ammonia concentration ($C_1 - C_2$) multiplied by the volume of the treatment unit and number of hydraulic retention times per day gives the ammonia emission rate in g/day. From the pond geometry, the volume equals 1.6 x 10^3 m^3, thus the ammonia emission rate (dm_A/dt) is calculated as follows:

$$\frac{dm_A}{dt} = (3.0\ \text{g/m}^3 - 1.2\ \text{g/m}^3)(1.6 \times 10^3\ \text{m}^3)(1/\text{day})$$

$$\frac{dm_A}{dt} = 2.88 \times 10^3\ \text{g/day} = 1.1 \times 10^3\ \text{kg/yr}$$

Methyl parathion annual production is estimated to be 23.1 x 10^3 metric tons (2), and the resulting emission factor due to ammonia desorption becomes 4.76 x 10^{-2} kg/metric ton.

APPENDIX B

EMISSION FACTORS USED IN PRIORITIZATION

This appendix presents the emission factors, emission species, and subjective data quality used to prioritize 80 major pesticides. Emission factors, as kg pollutant/metric ton pesticide, are listed in tablular form in Table B-1.

TABLE B-1. EMISSION FACTORS USED IN PRIORITIZATION

	Material emitted, kg/metric ton						
Source type	Particulate	SO_x	NO_x	Hydrocarbon	Carbon monoxide	Other	Data quality
Alachlor				1.5			D
Aldicarb		205		1.5		0.5 Aldricarb	D
Atrazine				1.5			D
Azinophos-ethyl		0.16	0.13	0.75		0.5 Ethion	D
Azinophos-methyl		0.16	0.13	0.75		0.5 Guthion	D
Bacillus thuringiensis	0.5						D
Benefin	0.96	1.28	0.96			3.2 Hydrogen chloride 0.32 Hydrogen fluoride	D
Bromacil				0.5		1.0 Hydrogen bromide 0.5 Bromine	D
Butachlor				1.5			D
Butylate		205		1.5		0.5 Butylate	D
Cacodylic acid						3×10^{-8} Arsenic trioxide 0.05 Methyl chloride 0.05 Methyl ketone 0.05 Methanol	D
Calcium acid methanearsonate						3×10^{-8} Arsenic trioxide	D
Calcium arsenate						3×10^{-8} Arsenic trioxide	D
Captafol						0.066 Captafol 1.0 Butadiene 0.5 Carbon disulfide	C
Captan						0.066 Captan 1.0 Butadiene 0.5 Carbon disulfide	B
Carbaryl				1.5		0.5 Carbaryl	D
Carbofuran				1.5		0.5 Carbofuran	D
CDEC		205		1.5		0.5 CDEC	D
Chloramben						1.0 Hydrogen chloride 0.5 Chlorine	D
Chlordane				1.0		0.5 Hydrogen chloride	D
Chlorpyrifos		205				0.5 Dursban	D
2,4-D acid, salts, esters						1.0 2,4-Dichlorophenol 1.0 Chloroacetic acid 1.5 Ammonia	D
Dalapon						0.5 Hydrogen chloride 0.5 Propionic acid 0.5 Dalapon	D
DBCP				1.0		0.5 Hydrogen chloride	D
DDT						0.5 DDT 0.5 Chlorobenzene 0.5 Chloral 8.8×10^{-7} DDT (evaporation)	D
Diazinon		205				0.5 Diazinon	D
Dicamba				1.0		0.5 Hydrogen chloride	D
Dichloropropene				1.0		0.5 Hydrogen chloride	D
Dichlorovos				1.0		0.5 Dichlorovos	D
Dicofol						0.5 Dicofol 0.5 Chlorobenzene 0.5 Chloral	D
Dicrotophos				0.5		0.5 Dicrotophos	D
Dimethoate		0.32	0.27	1.5		0.5 Toluene 0.5 Dimethoate	C
Dinoseb	0.96	1.28	0.96	1.0			C
Disulfoton		205				0.5 Disulfoton	D
Diuron				0.5		0.5 Chlorine	D

Note.—Blanks indicate no emission estimates were made.

(continued)

TABLE B-1 (continued)

	Material emitted, kg/metric ton						
Source type	Particulate	SO_x	NO_x	Hydrocarbon	Carbon monoxide	Other	Data quality
DSMA				1.0		3×10^{-8} Arsenic trioxide 0.05 Methyl chloride 0.05 Methyl ketone 0.05 Methanol	B
Endosulfan				1.0		0.5 Hydrogen chloride	D
Endrin				1.0		0.5 Hydrogen chloride	D
EPTC		205		1.5		0.5 EPTC	D
Fensulfothion		205				0.5 Fensulfothion	D
Flumeturon				0.5		0.5 Fluorine	D
Folpet						0.066 Folpet 1.0 Butadiene 0.5 Carbon disulfide	C
Heptachlor				1.0		0.5 Hydrogen chloride	D
Hexachlorobenzene				1.0		0.5 Hydrogen chloride	D
Lead arsenate						3×10^{-8} Arsenic trioxide	D
Lindane				1.0		0.5 Hydrogen chloride	D
Linuron				0.5		0.5 Chlorine	D
Malathion		0.32	0.27	1.5		0.5 Toluene 0.5 Malathion	C
Maneb		205		1.5		0.5 Maneb	D
Merphos		205					D
Metalkamate				1.5		0.5 Metalkamate	D
Methane arsenic acid						3×10^{-8} Arsenic trioxide	D
Methyoxychlor						0.5 Methoxychlor 0.5 Anisole	D
Methyl bromide						1.0 Hydrogen bromide 0.5 Bromine 0.5 Methyl bromide	D
Methyl parathion		410				1.0 Methyl parathion 1.0 Methyl alcohol 4.76×10^{-2} Ammonia (evaporation) 7.4×10^{-6} Methyl parathion (evaporation)	B
Mevinphos				0.5		0.5 Mevinphos	D
Monocrotophos				0.5		0.5 Monocrotophos	D
Monuron				0.5		0.5 Chlorine	D
MSMA				1.0		3×10^{-8} Arsenic trioxide 0.05 Methyl chloride 0.05 Methyl ketone 0.05 Methanol	B
Nabam		205		1.5		0.5 Nabam	D
Naled				0.5		0.5 Naled 0.5 Bromine	D
Parathion		410				1.0 Parathion 1.0 Ethyl alcohol 0.88 Ammonia (evaporation) 1.4×10^{-2} Parathion (evaporation)	B
Pentachlorophenol and sodium salts						0.55 Pentachlorophenol 2.2 Sodium pentachlorophenol 1.0 Phenol 1.0 Hydrogen chloride 0.5 Chlorine	B
Phorate		205				0.5 Phorate	D
Phosphamidion				0.5		0.5 Phosphamidion	D
Propachlor				0.5			D
Propanil				0.5			D
Propazine				1.5			D
Pyrethins	0.5			0.5			D
Ronnel		0.32	0.27	1.5		0.5 Toluene 0.5 Ronnel	D
Silvex						1.0 Phenol 0.5 Trichlorophenol 1.0 Hydrogen chloride	D
Simazine				1.5			D
Sodium TCA				1.0		0.5 Hydrogen chloride	D
TEPP				0.5		0.05 TEPP	D
Terbacil				0.5		1.0 Hydrogen chloride 0.5 Chlorine	D
Toxaphene						2.65 Hydrogen chloride 0.05 Chlorine 1.0 α-Pinene 5×10^{-6} Toxaphene 0.28 Toxaphene (evaporation)	C
Trichlorophenols						1.0 Phenol 0.5 Trichlorophenol 1.0 Hydrogen chloride	C
Trifluralin	0.96	1.28	0.96			3.2 Hydrogen chloride 0.32 Hydrogen fluoride	B
Vernolate		205		1.5		0.5 Vernolate	D
Zineb		205		1.5		0.5 Zineb	D

Note.—Blanks indicate no emission estimates were made.

GLOSSARY

active ingredient: Substance contained in a preparation which will by itself act in the same manner and for the same purposes as the directions provide for the preparation as a whole.

attractant: Substance which lures insects from distances to traps or poison bait stations. The most successful lures, when available, are the specific secretions of a particular insect species or their synthetic chemical equivalent (pheromone).

biological control: Parasitic and predaceous insects and insect disease organisms which are reared and disseminated artifically. Biological control includes the use of insects to control certain weeds as well as the use of any other living organism in fighting pests.

cholinesterase: Body enzyme necessary for proper nerve function that is destroyed or damaged by organophosphates or carbamates taken into the body by any path of entry.

encapsulated pesticides: Pesticides enclosed in tiny capsules that control release of the chemical and extend the period of diffusion, thus providing increased safety to applicators as well as the environment.

formulation: Pesticidal substances commercially mixed with other ingredients, such as carriers, diluents, solvents, wetting agents, emulsifiers, etc., because the chemicals are usually too concentrated and immiscible with water to be prepared directly for use by the purchaser.

juvenile hormone: Hormone produced by an insect in the process of its immature development which maintains its nymphal or larval form. Synthetic hormones or similar synthetic chemicals act as insecticides to control insects by preventing their maturity.

preemergence herbicide: Herbicide applied after planting the crop, but before the crop emerges above ground, in order to kill weed seedlings that appear ahead of the crop.

pyrethroids: Synthetic pyrethrin-like compounds produced in an attempt to duplicate the natural insecticidal activity derived from pyrethrum flowers.

systemic pesticide: Pesticide that is translocated to parts of a plant or animal other than those to which the material is applied.

CONVERSION FACTORS AND METRIC PREFIXES (29)

CONVERSION FACTORS

To convert from	To	Multiply by
Degree Celsius (°C)	Degree Fahrenheit	$t^\circ_F = 1.8\, t^\circ_C + 32$
Gram/kilogram (g/kg)	Pound/ton	1.999
Kilogram (kg)	Pound-mass (avoirdupois)	2.205
Kilogram (kg)	Ton (short, 2,000 lb mass)	1.102×10^{-3}
Kilometer (km)	Mile	1.609
Kilometer^2 (km^2)	Acre	2.470×10^{2}
Meter (m)	Foot	3.281
Meter^2 (m^2)	Foot^2	1.076×10^{1}
Meter^3 (m^3)	Foot^3	3.531×10^{1}
Metric ton	Pound	2.205×10^{3}
Pascal (Pa)	Inches of Hg (60°F)	2.961×10^{-4}

METRIC PREFIXES

Prefix	Symbol	Multiplication factor	Example
Kilo	k	10^{3}	1 kg = 1×10^{3} grams
Milli	m	10^{-3}	1 mm = 1×10^{-3} meter
Micro	μ	10^{-6}	1 m = 1×10^{-6} meter

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(29) Standard for Metric Practice. ANSI/ASTM Designation E 380-76$^{\varepsilon}$, IEEE Std 268-1976, American Society for Testing and Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.